

NASA Contractor Report 178413

DEVELOPMENT OF AN IMPACT- AND SOLVENT-RESISTANT THERMOPLASTIC COMPOSITE MATRIX — PHASE IV

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(NASA-CR-178413) DEVELOPMENT OF AN IMPACT- AND SOLVENT-RESISTANT THERMOPLASTIC COMPOSITE MATRIX, PHASE 4 (Acurex Corp.)
118 p CSCL 11D

N88-14145

G3/24 Unclass 0114269

Co.

September 1987

NASA

National Aeronautics and
Space Administration

Langley Research Center
Hampton, Virginia 23665-5225

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Contract No. NAS1-16808
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FOREWORD

This report was prepared by Acurex Corporation for the National Aeronautics and Space Administration, Langley Research Center, under contract NAS1-16808. The work was conducted from September 1985 to September 1987. Use of commercial products or names in this report does not constitute official endorsement of such products or manufacturers, either expressed or implied by the National Aeronautics and Space Administration.

Future aerospace vehicles may require the use of graphite composites with a favorable combination of properties including impact resistance. Thermoplastic resins provide composites with high-impact resistance. However, the solvent resistance of most thermoplastics is poor. Program efforts were directed towards the optimization of a solvent-resistant thermoplastic polyimide that would be amenable to the fabrication of high-quality composites.

Mr. Paul Hergenrother was the NASA technical monitor. The Materials Development Department of Aerotherm Division of Acurex Corporation performed the work on this contract. Mr. C. B. Delano was the program manager and Mr. C. J. Kiskiras provided technical assistance.

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SUMMARY

This 18-month follow-on Phase IV effort primarily addressed tailoring the melt viscosity properties of aliphatic-aromatic polyimides to give readily processable prepregs for manufacture of high-quality composites.

Since 93°C tensile testing of the polyimide from 3,3',4,4'-benzophenonetetracarboxylic dianhydride with 1,6-hexanediamine and m-phenylenediamine indicated during Phase III that shear yielding had occurred, initial efforts on this follow-on program were directed toward reducing the amount of the linear aliphatic portion of the polyimide. Substitution of the 1,6-hexanediamine with both 1,4-butanediamine and 1,3-bis(aminomethyl) cyclohexane gave the expected improvements in Barcol hardness at 93°C. The polyimide from the latter aliphatic diamine was selected for molecular weight/melt viscosity optimization efforts.

Reducing the molecular weight of the candidate polyimide by stoichiometric imbalance or end capping with phthalic anhydride led to insoluble material. Numerous unsuccessful attempts were made to find reaction conditions to eliminate formation of the insoluble material obtained upon evaporation of the solvent (m-cresol) from polymers prepared using 97.5 percent stoichiometry. Polymer from clear solutions isolated with methanol provided material with low pressure flow properties. However, redissolution of this same material in cresol and evaporation of the cresol gave a material that did not flow well.

By substituting 2,4-diaminotoluene for the m-phenylenediamine in the polyimide, low-pressure flow properties were obtained. The expected direct relationship between melt viscosity and molecular weight was obtained for the polyimide from 3,3',4,4'-benzophenonetetracarboxylic dianhydride with 2,4-diaminotoluene and 1,3-bis(aminomethyl)cyclohexane or 1,6-hexanediamine.

Polymers containing the 2,4-diaminotoluene were found to be soluble in chloroform, whereas polymers with m-phenylenediamine were not soluble. Since the objective of this follow-on effort was good melt processability, polymers containing the 2,4-diaminotoluene were used in the remaining efforts.

Polymers with an inherent viscosity of 0.55 dl/g were selected for prepregging and composite fabrication studies. This inherent viscosity represents a Brookfield viscosity of approximately 33 Pa·S at 20 percent solids in m-cresol. Blending of polymer solutions prepared from synthesis of phthalic anhydride end-capped polymers was used to achieve this Brookfield viscosity in solutions used for prepregging. Zero void composites were readily fabricated from these solutions by pressing solventless prepregs to selected thicknesses at elevated temperature and less than 6.9 MPa pressure.

Composite flexural strengths in excess of 698 MPa (100 ksi) were obtained with carbon-fabric composites at room temperature and 93°C from two polyimide compositions. These excellent values are attributed to a change in failure mode from composites tested previously and is probably due to improved compression properties of the matrix resin.

ABSTRACT

Polyimides from BTDA with m-phenylenediamine and three aliphatic diamines were prepared in m-cresol and characterized. Characterization tests included compression strength and modulus, stressed solvent resistance, and melt-flow tests. Efforts to reduce the molecular weights of these polymers by either stoichiometric imbalance or phthalic anhydride end capping produced opacity in the polymer moldings when the stoichiometry was less than 99 percent. Use of 2,4-diaminotoluene in place of the m-phenylenediamine allows clear polymer moldings to be obtained at all stoichiometries by end capping or stoichiometric imbalance. After melt-flow/molecular-weight studies, carbon fabric composites were prepared from three polyimide compositions containing BTDA, 2,4-diaminotoluene and two aliphatic diamines. Flexural strengths of two of the resins were in excess of 689 MPa (100 ksi) at both room temperature and 93°C. The polyimide from BTDA, 1,6-hexanediamine, 1,3-bis(aminomethyl)cyclohexane and 2,4-diaminotoluene was selected for scale-up and neat resin characterization tests. The T_g of this polymer was 233°C.

SECTION 1

INTRODUCTION

This report describes an 18-month follow-on effort conducted to develop improved thermoplastic resins for application in composite structures for aerospace vehicles. Section 1.1 describes the advantages of such a system, Section 1.2 briefly summarizes prior efforts,^{1,2} and Section 1.3 describes our approach to the follow-on effort.

1.1 BACKGROUND

The successful development of impact- and solvent-resistant thermoplastic systems for glass and graphite composites is particularly attractive from the standpoint of their potential low-cost and streamlined manufacturability. Hypothetically, thermoplastics only require simple heating and cooling cycles for component manufacture, whereas thermosets require more precise, and possibly extended, heating schedules which must be consistent with the cure chemistry.

High modulus (matrix properties), excellent processability, and solvent resistance (high crosslink density) are some of the attractive features of thermosets, which are currently the preferred matrices for graphite composites. Furthermore, since the B-staged epoxy resins are liquids, excellent fiber collimation is achievable in the prepregs. The response of graphite composites to low-speed impact has been of concern for a number of years. Kevlar, glass, and other fibers are used with graphite fibers to

provide more impact-resistant composites. Such "hybrids" compromise initial mechanical properties (modulus, compressive strength) to provide improved impact properties. Thermoplastics, on the other hand, offer impact resistance not attainable with conventional thermosets (excludes new toughened systems).

Aircraft design requires lifetime prediction of their components. Any material which exhibits environmental degradation will compromise the design safety margins for the selected component. Conventional thermosets absorb moisture which lowers their performance, especially at elevated temperatures.

The sensitivity of existing thermoplastics to aircraft fluids and other solvents may preempt their serious consideration in aircraft components. Therefore, Acurex proposed resistance to aircraft solvents as the starting point for the program effort. Exposure to fuel, deicing fluids, and hydraulic fluids are serious concerns. Methods to remove paint from composites are being examined by a number of investigators. If successful, use of paint strippers on composites may not be required.

1.2 PRIOR EFFORTS

The Acurex approach is based on the development of polymers with rigid crystallizable segments interconnected with soft or flexible, energy-absorbing segments. The rigid segments can act as physical crosslinks between polymer chains and provide high-modulus and solvent resistance. The interconnecting soft segments provide impact resistance and melt processibility.

The excellent common solvent resistance under stress of three polyaliphatic-aromatic heterocyclics (two polyimides and polybenzimidazole) verified the soft-rigid segment approach to obtaining solvent-insensitive polymers. The polyimide from 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) with 1,8-octanediamine (ODA), and m-phenylenediamine (m-PDA) was selected as the best candidate from the first-year Phase I effort.

The second-year Phase II efforts continued to show promise for this polymer. However, due to opacity developed in the molded polymer with 1-hr treatment at 316°C (600°F), 1,6-hexanediamine (HDA) was substituted for the ODA since that composition remains clear with the cited thermal treatment. It should be noted that these selections were based on a number of factors which are consistent with current understanding of composite resins, e.g., good tensile properties of the bulk resin. These efforts are described in NASA CR 172285.1

Methods to produce carbon-fiber prepregs which would produce high-quality composites from the selected polyimide were addressed in the third-year Phase III effort. Amenability to fiber impregnation using conventional equipment was addressed in depth. Other Acurex efforts suggested that low-solids content varnishes of polyphenylquinoxaline and polysulfone can be used to prepare carbon-fiber prepregs and composites. In the first months of the Phase III effort, it was determined that low-solids content cresol solutions of the high-molecular weight BTDA/HDA/m-PDA polyimide provided composites with incompletely impregnated fiber bundles. The interply resin in these 6.9 MPa processed composites, however, was void free. Excellent fiber bundle impregnation was achieved by the use of monomers and prepolymers to produce >50 percent solids content impregnating varnishes. With the fiber bundles filled, the resin content at the prepregs surface was reduced and high-pressure molding of such prepregs did not always produce void-free composites. Voids were most evident in the interply regions suggesting a need for more resin on the prepreg surface. It was concluded that high-fiber volume, thermoplastic prepregs made by this method should be completely smooth and dense for the fabrication of quality composites.

Conditions were developed for the production of smooth and dense prepregs using high pressures (13.8 MPa). Numerous attempts to produce the prepreg at atmospheric pressure with varying thermal, squeegeeing, and smoothing schedules invariably led to a high-melt viscosity varnish which, after final volatile removal, required high pressures for final perfecting of the prepreg. Processing the prepregs under vacuum and heat provided perfected prepregs at lower pressures. However, commercial prepregs are not currently produced with vacuum treatment.

The need to use the preimidized aliphatic diamine prepolymer in prepregging varnishes was also established to reduce the moisture sensitivity of the prepregs. The melt viscosity requirements of 100 percent solids neat resins to produce perfected prepregs needed additional study. The uncontrolled molecular weight growth that generally occurs in condensation polyimides will not be amenable to reproducible prepreg production or low-pressure composite processing. Injection-moldable thermoplastics have controlled flow properties.

The BTDA/HDA/m-PDA polyimide (neat resin) is moldable at 0.69 MPa and temperatures as low as 260°C. However, it became evident that the neat resin must be capable of being molded at a far lower pressure than 0.69 MPa to provide prepreg which can be molded into composites at 0.69 MPa due to the restriction of the resin's flow by the fibers. These efforts are described in NASA CR 172568.² The shortcoming of resins with low-flow properties is shown in Figure 1. Final smoothing of the prepreg must occur after volatile removal and use of resins with lower melt viscosities is required.

1.3 PRESENT EFFORTS

Present efforts concerned optimization of the melt flow properties of the polyimide to obtain low-void composites, a subject prior efforts had not

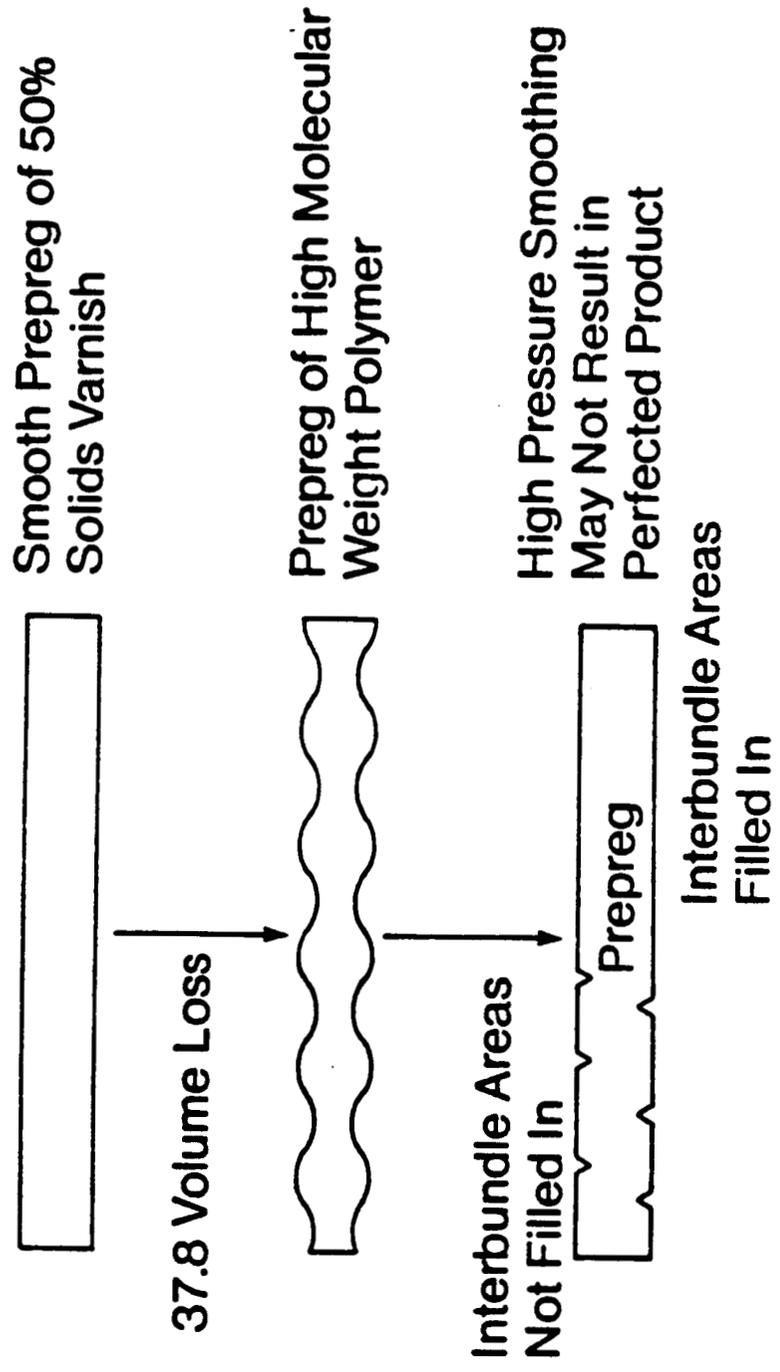


Figure 1. Resin shrinkage and smooth preregs

addressed. Melt viscosity is directly related to the polymer's molecular weight and therefore molecular weight tailoring of the candidate polyimide to achieve lower melt viscosity was the approach taken.

The room temperature strengths of unannealed composite and neat resin specimens from the BTDA/HDA/m-PDA polyimide were excellent. However, strength loss appeared to be more rapid for the polyimide at elevated temperatures than state-of-the-art 177°C curing epoxy systems. This loss of properties at elevated temperatures is attributed to shear yielding.

Initial efforts on the present program addressed substitution of the HDA with two alternative aliphatic diamines. Reducing the length of the flexible aliphatic segment, for example, from HDA to 1,4-butanediamine (BDA), was expected to lead to improved elevated temperature composite strengths. 1,3-Bis(aminomethyl)cyclohexane (BAC) was also selected for investigation.

As noted in Figure 2, plotting Barcol hardness values against the percent by weight of the linear aliphatic portion of numerous polymers shows the validity of the approach (assumes a relationship between Barcol hardness and compression strength). The cyclohexane ring in the BTDA/BAC/m-PDA polymer is treated as a rigid backbone segment. The polymer compositions are indicated in Table 1. Glass transition temperatures (T_g) of the polymers are also given in Figure 2 and Table 1.

The improvement in Barcol hardness of the BTDA/BDA/m-PDA and BTDA/BAC/m-PDA polymers over the BTDA/MDA polymer is apparent. This improvement is attributed to the use of m-PDA in the polymers and in the case of the BTDA/BAC/m-PDA polymer, use of the 1,3 isomer of the bis(aminomethyl) cyclohexane which would also give a "meta" effect. The Barcol hardness of an Acurex-prepared MY720/DDS sample is 55³ and the BTDA/BAC/m-PDA polymer has almost this hardness, suggesting that it holds potential to provide excellent

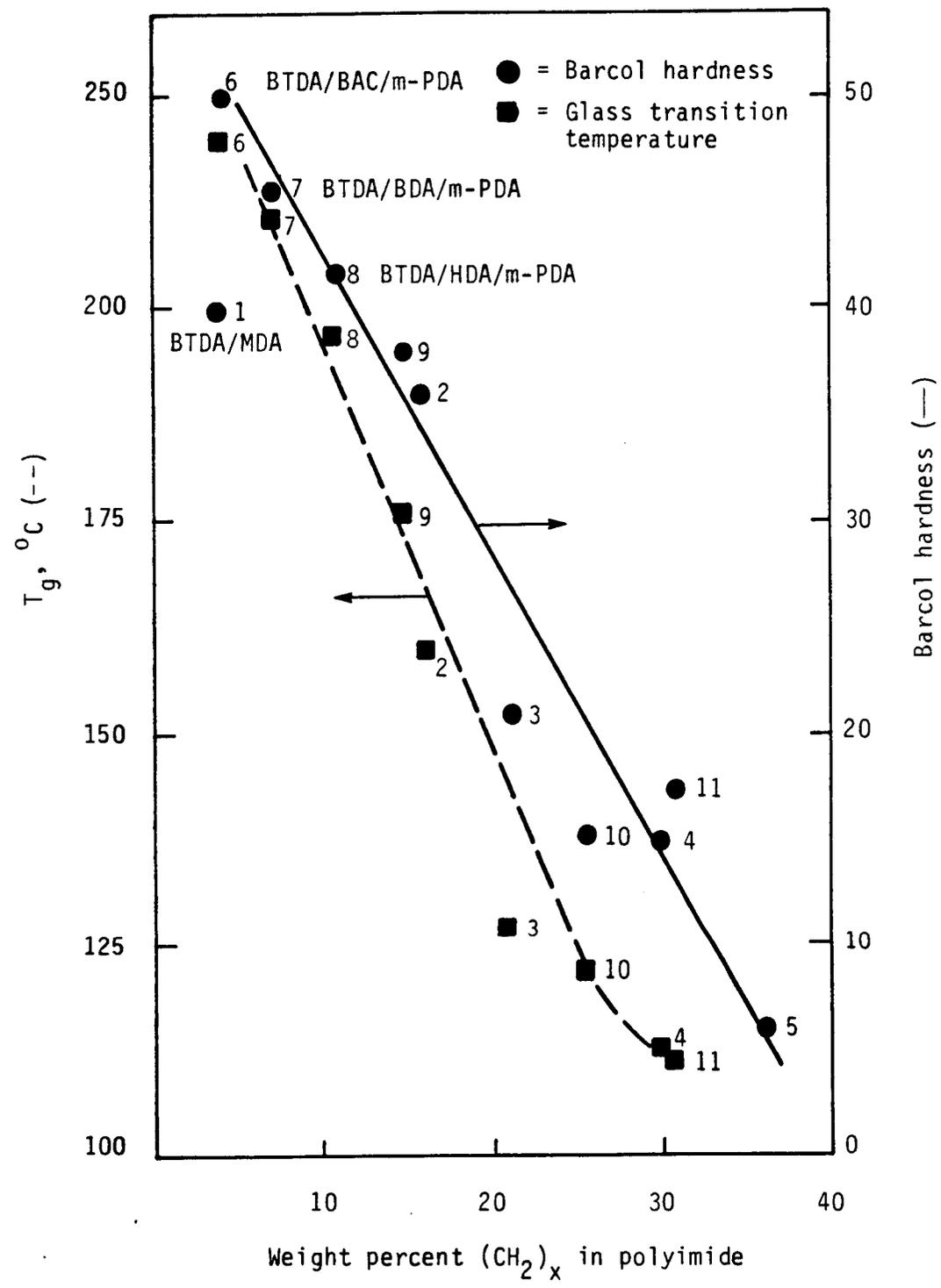


Figure 2. Weight percent flexible segment versus Barcol hardness

Table 1. Glass transition temperature and Barcol hardness of molded polymer samples

Number	Polymer Composition ^a	T _g , °C	Barcol Hardness		
			RT Test	93°C Test	140°C Test
1	BTDA with MDA	296	40	31	32
2	BTDA with BDA	160	36	30	19
3	BTDA with HDA	127	21	12	0
4	BTDA with ODA	113	15	0	0
5	BTDA with DDA	89	6	0	0
6	BTDA ^b with BAC and m-PDA	241	50	45	39
7	BTDA ^b with BDA and m-PDA	222	46	40	33
8	BTDA ^b with HDA and m-PDA	196	42	35	30
8A	BTDA with HDA and m-PDA	200	38	26	18
9	BTDA with ODA and m-PDA	176	38	21	13
10	BTDA and PMDA with HDA	117	15	0	0
11	BTDA and PMDA with ODA	111	17	0	0

^aBTDA = Benzophenonetetracarboxylic dianhydride

BMDA = Pyromellitic dianhydride

MDA = 4,4'-methylenedianiline

BDA = 1,4-butanediamine

HDA = 1,6-hexanediamine

ODA = 1,8-octanediamine

DDA = 1,12-dodecanediamine

BAC = 1,3-Bis(aminomethyl)cyclohexane

m-PDA = m-phenylenediamine

^bBTDA from the Chriskev Company

composite strengths. As a consequence, molecular weight/melt viscosity efforts were conducted on the BTDA/BAC/m-PDA polyimide after it was selected from initial efforts on the present program.

SECTION 2

OBJECTIVE

The overall objective of this program is the development of new thermoplastic laminating resin(s) that can be used with glass or graphite fibers to provide impact- and solvent-resistant composites for potential use on aerospace vehicles. These composites must have mechanical properties equivalent to state-of-the-art 177°C (350°F) curing epoxy systems. Although several routes can be pursued to improve the impact strength of composites (such as increasing the strain-to-failure capability of the reinforcement) this effort specifically pertains to resin development. Even though the tensile strength and tensile modulus of the reinforcement are considered to be the dominant contributors to impact strength of composites, the matrix also plays an important role by transferring load and dissipating stress.

Target properties for the polymers are listed below.

- Amenable to impregnation of a reinforcement using conventional equipment
- Long prepreg shelf life at ambient conditions (>6 months)
- Acceptable processibility [maximum curing temperature of 316°C (600°F), maximum curing pressure of 0.69 MPa (100 psi), maximum time at final temperature of 1 hr, insensitive to heatup rate, and no volatile evolution]

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- Thermoformability (thermoform flat-sheet stock to desired configurations at maximum temperature and pressure of 316°C and 0.69 MPa, respectively; ability to undergo thermoforming process twice)
- Acceptable mechanical properties over temperature range of -54° to 93°C (-65° to 200°F) after environmental exposure (humid aging and long-term aging at 93°C)
- Resistant to airplane fluids and solvents (under stress)
- Impact resistance and damage tolerance

SECTION 3

RESULTS AND DISCUSSION

This section has been divided into subsections which deal with different key aspects of the development effort. Initial efforts were directed toward selection of the best of three candidate polymers based on a number of tests. These efforts are described in Section 3.1, Polymer Selection. The BTDA/BAC/m-PDA polymer was selected for molecular weight/melt flow optimization studies. These studies ensued and are described in Section 3.2, Molecular Weight/Melt Flow Optimization Studies. Composite efforts are described in Section 3.3.

3.1 POLYMER SELECTION

3.1.1 Synthesis

Initial efforts required preparing three polymers in sufficient quantity and molecular weight to select the one with the best balance of properties for further evaluation. The three polymers were from BTDA and m-PDA with three aliphatic diamines, BDA, HDA, and BAC. These efforts are described below.

Monomers

BDA, HDA, and 2,4-diaminotoluene (2,4-DAT) were used in the as-received condition from materials which had been successfully polymerized in the past. The m-PDA was distilled at 0.3 mm Hg at 110°C. The BAC was vacuum distilled and the four fractions analyzed by gas chromatography. The first fraction had

an obvious low boiling contaminate. The last three fractions had a trace of the same low boiling contaminate which was not removed by the simple distillation. If required, a column could be used to possibly remove this contaminate. However, as evidenced by the inherent viscosities (IVs)* obtained from the polymerizations discussed below, this small amount of contaminate does not appear to limit molecular weight growth.

BTDA was initially used in the as-received condition from the Chriskev Company. A subsequent lot of this material had the distinct odor of acetic anhydride. Therefore, subsequent lots were treated overnight in a vacuum oven at 180°C prior to use.

BTDA from the Chriskev Company is imported from Japan and is chemically dehydrated compared to thermal dehydration used on Gulf Chemical's† material. It is reported to be purer than the Gulf material and free of triacid. Its anhydride assay by aniline titration is 98.6 percent. The remaining 1.4 percent is tetraacid.

As discussed in the next section, initial difficulty in obtaining viscous cresol solutions of the polymer from BTDA with BDA and m-PDA prompted distillation of the BDA and gas chromatographic analysis of the various fractions. The as-received BDA was of good purity and after distillation at 160.0° to 160.8°C, the last two cuts were nearly chromatographically pure and were combined. This higher purity BDA also failed to provide viscous cresol solutions of polymer.

As discussed below, there is a significant difference in the polymerizability of BTDA from the two sources. Gulf's BTDA provides high

*All IV's in this report were conducted in cresol at 25.0°C at 0.5 g/100 ml concentration.

†Now Alco. Alco also has available high-purity BTDA which was not tested in the present program.

molecular-weight polymers in cresol in 1 to 2 hr at 180°C whereas Chriskev's BTDA requires overnight reaction at 180°C to obtain high molecular-weight polymers.

BTDA/BDA/m-PDA Polymer

The BTDA/BDA polymer had been successfully prepared during prior efforts by a standard method which involved a final reaction condition of 1 hr at 180°C. After four unsuccessful attempts to obtain viscous cresol solutions of the BTDA/BDA/m-PDA polymer after 1 hr at 180°C, efforts shifted to the BTDA/HDA/m-PDA polymer. New methods to prepare the BTDA/HDA/m-PDA polymer were developed, and used to prepare the BTDA/BDA/m-PDA polymer.

The BTDA/BDA/m-PDA polymer was successfully prepared as follows: After the BTDA was dissolved in cresol at 180°C, the solution was placed in an ice bath. A cresol solution of BDA was added to the cold BTDA-cresol solution. After 30 min at room temperature, the BTDA/BDA prepolymer was heated for 2 hr and 20 min in a 180°C oil bath followed by cooling to room temperature. A m-PDA-cresol solution was added, adjusting the solution to 10 percent solids content. Based on the monomer weights, 99.50 percent of the stoichiometric diamine weights had been added. The reaction was then immersed into an 180°C oil bath. After 2 hr and 16.5 hr, IVs of aliquots withdrawn from the reaction were 0.30 and 0.37 dl/g respectively. The m-PDA was then added to the polymerization to give a calculated stoichiometry of 100.20 percent. After 4 more hours of reaction at 180°C, the IV of a sample of the polymer was 0.48 dl/g. After final addition of m-PDA to give a calculated diamine stoichiometry of 101.00 percent and 20 hr reaction time at 180°C, the IV of the polymer was 1.02 dl/g. The polymerization was viscous and clear at the 180°C reaction temperature. Additional 24-hr and 48-hr reaction periods at 180°C produced polymer samples with IVs of 1.22 and 1.31 dl/g, respectively.

A 239g batch of the BTDA/BDA/m-PDA polymer was successfully prepared following the procedure described above. After condensation of the BTDA/BDA prepolymer for 2 hr at 180°C, a cresol solution of m-PDA was added to give a calculated total amine stoichiometry of 100 percent. The polymerization solids content was adjusted to 12 percent and the reaction heated to 180°C. After 4 hr at 180°C, the IV of the polymer was 0.53 dl/g. The amine stoichiometry was increased to 100.80 percent and, after a 4-hr additional reaction at 180°C, the IV of the polymer was 1.05 dl/g.

This polymer was isolated by slowly pouring the cresol solution into a Waring blender containing methanol. The isolated polymer was stirred for 30 min in refluxing isopropyl alcohol, filtered, and finally dried 16 hours at 170°C and 0.1 mm Hg. This polymer was used to make the moldings required for mechanical property determinations and other tests.

Additional polymer was required so 61g were prepared from the same raw materials employed above (a different lot of BTDA). After precondensation of the BTDA/HDA prepolymer for 12 hr at 180°C, the amine stoichiometry was adjusted with m-PDA to 100.81 percent and the solids content was adjusted to 15 percent. After 4-hr and 8-hr reaction times at 180°C, the IV of the polymer was 0.67 dl/g and 1.32 dl/g, respectively. The polymer solution at the reaction temperature was very viscous and was diluted to 10 percent solids prior to isolation in methanol.

BTDA/HDA/m-PDA Polymer

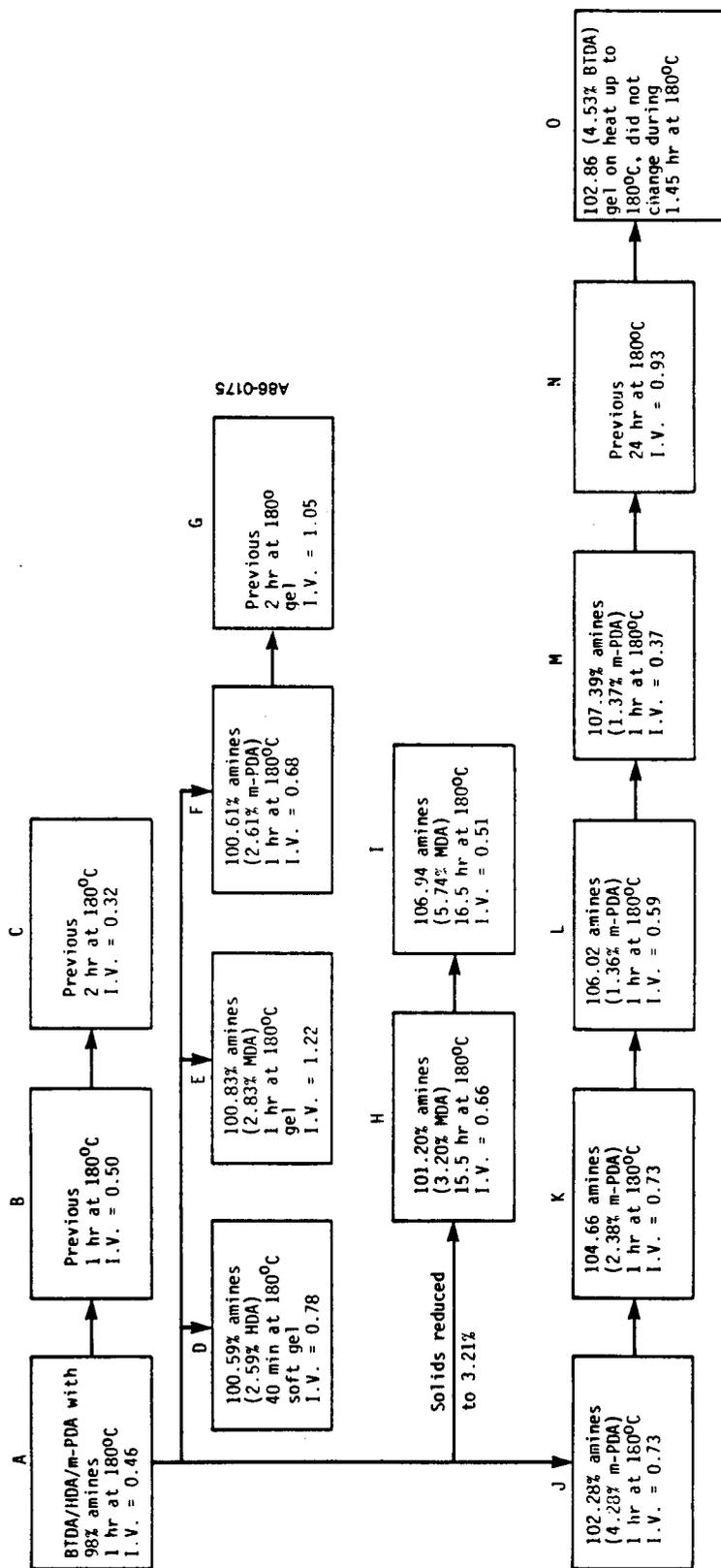
The reactions described below were conducted on the BTDA/HDA/m-PDA polymer after the preliminary experiments with the BTDA/BDA/m-PDA polymer failed to provide high molecular-weight polymer. Based on prior polymerizations, aliphatic or aromatic diamines added above stoichiometric quantities usually resulted in a gel, presumably due to crosslinking reactions.

As a prelude to attempt to polymerize BTDA with HDA and m-PDA, the polymerizability of BTDA was tested with HDA. Thus, BTDA with a 95 percent stoichiometric quantity of HDA, was heated for 1 hr at 180°C in cresol at 10.69 percent solids. The additions of 1.6 percent HDA and 2.0 percent HDA, each followed by a 1-hr reaction at 180°C, did not significantly increase the viscosity of the hot solution. The further addition of 5 percent HDA followed by treatment at 180°C led to a gel after 15 minutes at temperature. The stoichiometry at gelation was about 103.5 percent HDA. This gel is defined as a Type A gel which is caused by an addition of excess diamine to the polymerization and is probably attributable to interchain crosslinks with diamine molecules.

A 98.00 stoichiometric BTDA/HDA/m-PDA polymer was prepared at 11.71 percent solids in cresol. The m-PDA, added as a cresol solution at room temperature, was reacted with the BTDA/HDA prepolymer at 180°C for 1 hr and 35 min. The BTDA/HDA prepolymer solution was prepared by addition of a HDA-cresol solution to the ice-bath-cooled BTDA-cresol solution followed by condensation at 180°C for 1 hr and 15 min. Several aliquots of the reaction mixture were taken for further reaction with m-PDA and other diamines to investigate reaction conditions required to produce high-molecular-weight polymer.

Reaction conditions, calculated final stoichiometries, and resulting IVs are indicated in Figure 3. The following observations were made from Figure 3.

- At 100.5 percent stoichiometric amine, HDA and MDA lead to gel in 1/3 of the time it takes m-PDA to gel (Figure 3, Blocks D, E, F, and G)
- Excess MDA or m-PDA does not necessarily lead to gel (Figure 3, Blocks H and I, and the Blocks, J, K, L, M, and N)



Notes:

1. Polymerizations at 11.71% solids unless noted otherwise
2. I.V. = inherent viscosity in cresol at 0.5 dl/g at 25°C
3. MDA = 4,4'-methylenediamine, HDA = 1,6-hexanediamine, and m-PDA = m-phenylenediamine
4. Total time at temperature is sum of indicated reaction time
5. See Section 5 for details

Figure 3. Inherent viscosity/stoichiometry studies with the BTDA/HDA/m-PDA polymer

- Excess m-PDA appears to cleave the backbone (Figure 3, Blocks K, L, and M); however, overnight reaction lead to a significant increase in the IV of one polymer containing excess m-PDA (Figure 3, Blocks M and N)

The study described above raises more questions than it answers, particularly in view of the fact that all three gels obtained at about 100.5 percent stoichiometry were found to be soluble in excess cresol after overnight heating at 60°C (Figure 3 blocks D, E, and F). This type of gel is defined as a Type B gel. As to whether Type A gels can be diluted to obtain soluble polymer and thus become a Type B gel is unknown since most gels in the past have been discarded and not tested for slow dissolution in cresol at 60°C.

Results from a second polymerization similiar to the one described above are shown in Figure 4.

Observations from the reactions and samples removed are listed below.

- The 100.5 percent amine stoichiometry led to a gel as observed in the first study which could be slowly dissolved in cresol at 60°C for IV determination (Figure 4, Block E)
- A direct relationship exists between IV and solids content of the reaction

This latter relationship is plotted in Figure 5, and the relationship between the percent solids and IVs for the 20 hr at 180°C samples (22 hr total reaction time) suggests a second-order reaction. Oil bath temperature variation which affects the reaction rate was normalized by placing the samples in test tubes in the same stirred oil bath for the overnight reaction. Significant increases in the IVs were observed for all of the reactions. The attainment of a polymer with an IV of 1.36 dl/g without observing gel was

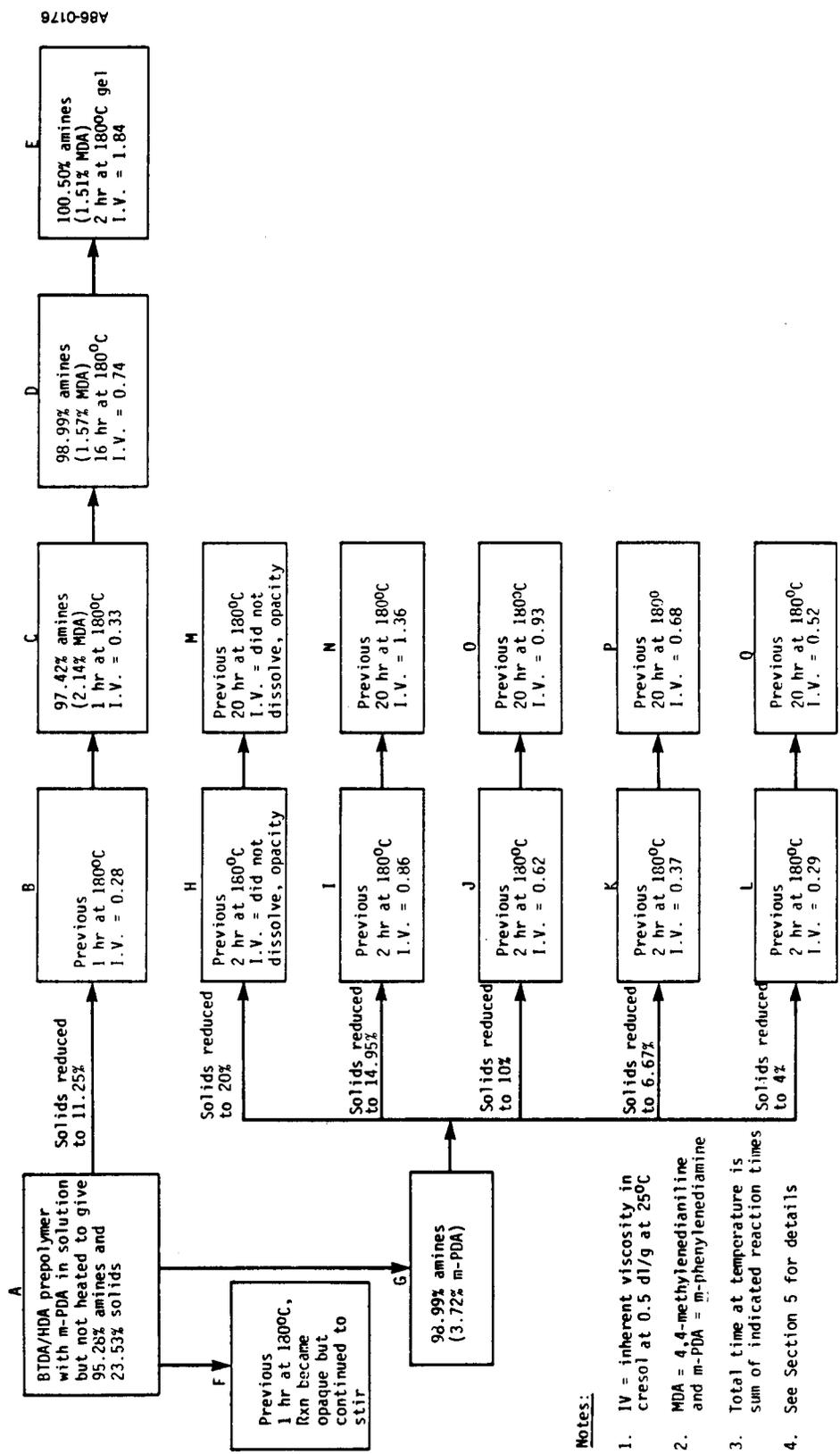
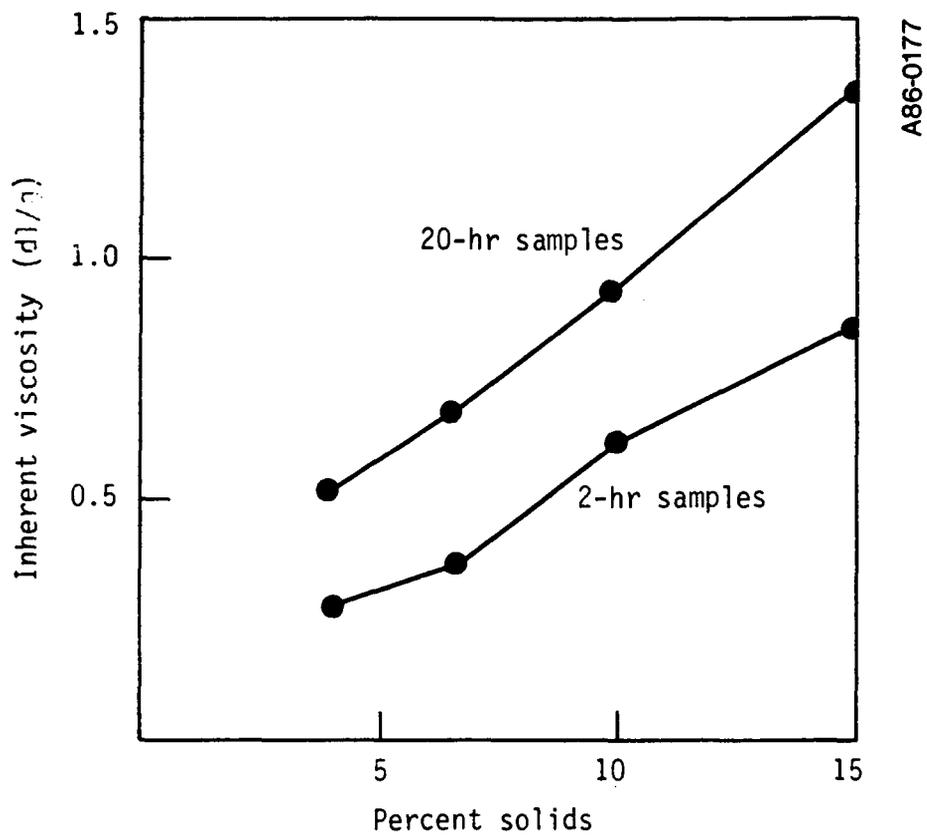


Figure 4. Inherent viscosity/reaction solids content studies with the BTDA/HDA/m-PDA polymer



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Note: 2-hr samples reacted individually with stirring. 20-hr samples all reacted in same oil bath in test tubes without stirring. (22-hr total reaction time, see Figure 4.)

Figure 5. Inherent viscosity versus percent solids

significant. All samples appeared to be in solution at the reaction temperature. However, an elastomeric behavior was observed in the cooled cresol solutions of the 10, 15, and 20 percent solids reactions. All of the reactions were clear up to 15 percent solids. At 20 percent solids, a slight haze developed in the second hour of reaction at 180°C and at 23 percent solids a heavy opacity developed in the first hour of reaction at 180°C.

It is noteworthy that prior efforts involved scale-up of the 99.0 percent stoichiometric amine reaction at 13 percent solids since the last 1.0 percent amine could not be added without gel formation. A 2-hr reaction at 180°C (1 hr at 96.0 percent amine stoichiometry and the last hour at 99.0 percent stoichiometry) resulted in IVs of about 1 dl/g (H₂SO₄). With the understanding that the rate of molecular-weight growth at 180°C is apparently slower with the Chriskev BTDA, the 1-hr reaction times at 180°C are obviously inadequate, particularly with m-PDA.

The second study, although key to understanding how to achieve high-molecular weight, poses more questions, i.e., can high-molecular-weight polymer be made at 98.0 percent amine stoichiometry and high solids content reactions?

A 247g polymerization of the BTDA/HDA/m-PDA polymer was prepared by procedures described above at 15 percent solids. After a 2-hr reaction at 180°C at 98.50 percent amine stoichiometry, the IV of the polymer was 0.53 dl/g. The reaction seemed to be slightly hazy. The amine stoichiometry was adjusted to 99.00 percent and after 12-hr reaction at 180°C, the IV of the polymer was 0.90 dl/g. The polymerization was hazy compared to the very clear solution obtained on the BTDA/BDA/m-PDA polymer described in the previous section. The polymer was isolated as previously described.

BTDA/BAC/m-PDA Polymer

An 8g polymerization at 99.95 percent amine stoichiometry and 15 percent solids was carried out as described in the previous sections. After 4- and 8-hr reaction times in a 180°C oil bath, the IVs of the polymers were 0.41 and 0.44 dl/g, respectively. The stoichiometry was adjusted to 101.00 percent with m-PDA followed by heating to 180°C for 15 hr. After 12 hr at 180°C, the polymerization was viscous but not gelled. After 15 hr the polymerization mixture was not stirrable but upon dilution to 10 percent solids, it became stirrable again. The IV of the polymer was 1.85 dl/g after the 15-hr reaction time at 180°C at the 101.00 percent amine stoichiometry.

A 255g polymerization was carried out at 15 percent solids and a total amine stoichiometry of 100.99 percent. After a 3-hr reaction at 180°C, the IV of the polymer was 0.47 dl/g. Additional reaction at 180°C for 3 hr produced a polymer with an IV of 0.69 dl/g and after 4 more hours of reaction the IV of the polymer was 0.90 dl/g. The polymer was then isolated by the previously described procedure.

3.1.2 Moldings of High-Molecular-Weight Polymers

Thick Moldings

Preliminary molding studies on 2g samples in a 5.1 cm² disk mold demonstrated that the three candidate polymers were completely molded at 6.9 MPa at the temperatures indicated below:

<u>Composition</u>	<u>Temperature</u>
BTDA/BDA/m-PDA	316°C
BTDA/HDA/m-PDA	288°C
BTDA/BAC/m-PDA	343°C

Since these initial molding efforts were directed toward mechanical property and other tests, other molding conditions were not investigated. The polymers were molded with a 10-min hold at the temperatures indicated above to produce several moldings.

Sixty gram samples of each polymer were molded to nominal thicknesses of 0.3 cm for G_{1C} testing. The moldings were quartered and two each of the opposite quadrants were transmitted to NASA in the "as molded" and "annealed" conditions. Annealing studies are discussed in the next section of the report.

Thirty gram samples of each polymer were molded to nominal thicknesses of 0.22 cm. These moldings were sectioned into 1.27 cm strips for solvent resistance and other tests.

One hundred gram samples of each polymer were molded to nominal 1.27-cm thicknesses for compression testing.

All of the above moldings appeared to be homogeneous by transmitted light and were good quality except for the 100g molding of the BTDA/BAC/m-PDA polymer which had entrapped air bubbles near the center of the molding. Only about 10 percent of the area of the molding contained the bubbles.

Thin Moldings

Attempts to mold tensile specimens thinner than the other moldings led to moldings from all three of the candidate polymers which contained 10 to 30 percent unmolded areas. These moldings were to have an areal weight of approximately 0.2 g/cm^2 , which is a factor of about 5 less than the next thicker moldings. Unmolded areas are a direct result of uneven polymer distribution in the mold, limited processibility of the polymers and accordingly uneven pressure distribution during the molding.

This problem was studied in some detail, even though moldability was not part of the decision matrix for selection of the best candidate. Perfected prepregs will probably have areal weights of less than 0.2 g/cm^2 . Furthermore, they will contain up to 65 volume percent fibers which will further arrest resin flow in the xy plane.

To investigate the inability of the resin to provide good quality thin moldings, unmolded fibrous resins (TGA scans showed that all three resins were essentially free of cresol) were placed into a 2.54 cm^2 plunger mold at about a 45° angle and molding pressure and temperature varied to determine conditions necessary to "fill" the mold. The areal weight of completely molded specimens was about 0.2 g/cm^2 . All three candidates required relatively high pressures to fill the mold.

The percent molded area for the 6.9 MPa (1000 psi), 303°C processed moldings are listed in Table 2. The mold was placed into a preheated press and pressure applied for 30 min with hold times in the mold prior to pressure application of 0, 10, and 30 min. Thermocouple readings indicated that the molding reached the temperature in about 15 min and was approximately isothermal for the remainder of the time. Lower pressure moldings, i.e., 1.4 MPa (200 psi), gave a smaller percentage molded area, as expected, which correlated with the reduced pressure. Thus the 1.4 MPa processed moldings had molded areas of about one-fifth of the 6.9 MPa processed moldings.

The percent molded areas indicated in Table 2 show that only one of the three candidate polymers "filled" the mold at the 6.9 MPa, 303°C molding conditions (BTDA/HDA/m-PDA polymer). Holds of 10 and 30 min in the heating mold prior to pressure application reduced the flow of the BTDA/HDA/m-PDA polymer and gave only a 90 percent molded area. Heating the BTDA/BDA/m-PDA

Table 2. Molding studies of the three candidate polymers at 303°C

Composition	Hold Time With No Pressure (min)	Time with 6.9 MPa Pressure (min)	Estimated Clear Molded Area (%)
BTDA/BDA/m-PDA ^a	0	30	80
	10	30	70
	30	30	60
BTDA/HDA/m-PDA	0	30	100
	10	30	90
	30	30	90
BTDA/BAC/m-PDA	0	30	70
	10	30	70
	30	30	70

^aTwo batches of polymer were tested with the same results obtained for both batches. Cresol IV's of the two batches were 1.05 and 1.32 dl/g

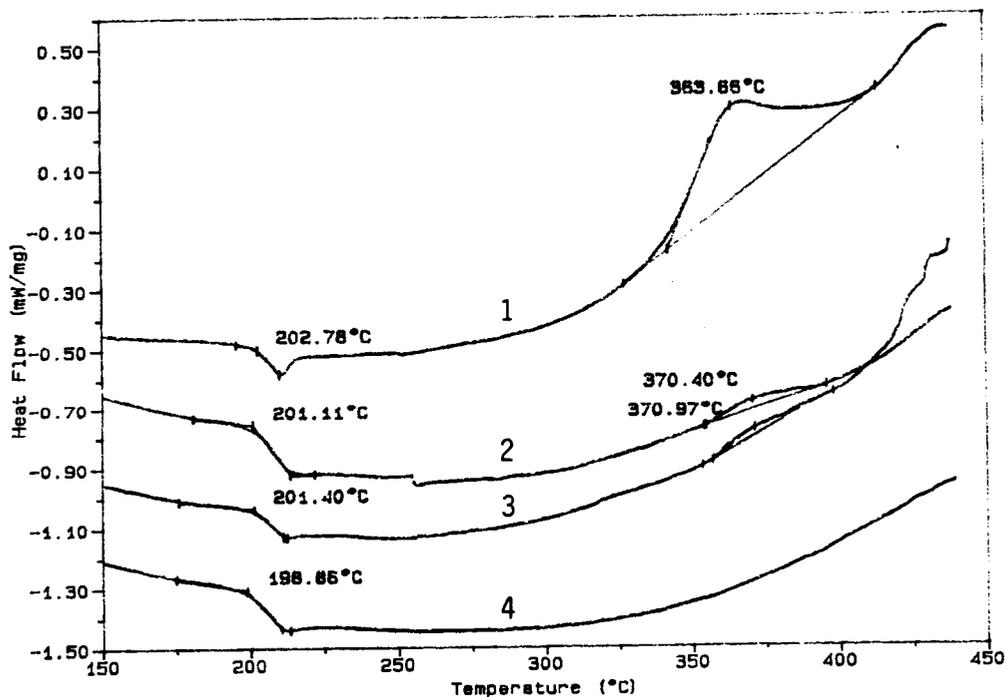
polymer prior to pressure application also led to reduced flow areas. The BTDA/BAC/m-PDA polymer gave constant flow areas with 0, 10, and 30 min holds prior to pressure application. Prior program efforts² with the BTDA/HDA/m-PDA polymer showed reduced flow with increasing molding temperature.

DSC Analysis of Molded and Unmolded Polymers

DSC analysis of molded and unmolded portions of the disks as well as virgin polymer and other moldings was carried out in an attempt to understand why reduced flow areas were observed with hold times at temperature prior to pressure application. Figure 6 provides DSC curves* of the BTDA/HDA/m-PDA polymer in three conditions: as prepared, molded 10 min at 288°C, and heated for 1 hr at 316°C after molding for 10 min at 288°C. The fourth curve is a reheat of the DSC sample (heated to 425°C), which was molded 10 min at 288°C. The T_g transition is evident, as well as a high-temperature exotherm which is nearly eliminated with molding and completely eliminated by treatment to 425°C. The exotherm associated with melt of the powder isolated from a cresol solution with methyl alcohol has been previously noted. It was concluded from inspection of numerous DSC traces that high temperatures (~425°C) eliminate the exotherm, and fusion under pressure and temperature conditions also eliminates the exotherm. Fusion alone, as evidenced by good clarity of the molding, does not eliminate the exotherm. The origin of the exotherm is unknown.

Table 3 summarizes the data on selected as-prepared polyimides. The suggestion that the peak exotherm temperature is a basic characteristic of the polymer's composition is noted. For example, the BTDA/BDA/m-PDA polymer, sample No. 48-83, isolated with methyl alcohol, has the same peak exotherm

*All DSC, TGA and other thermal analyses in this report were conducted at 15°C/min unless noted otherwise



Curves from top to bottom are:

- Curve 1 = As prepared fibers, $\Delta H = 40.4$ J/g
- Curve 2 = Molded 10 min at 288° , $\Delta H = 1.0$ J/g
- Curve 3 = Above plus 1 hr at 316° , $\Delta H = 0.9$ J/g
- Curve 4 = Reheat of sample which gave Curve 2

Tgs shown are onset temperatures

Figure 6. DSC analysis of BTDA/HDA/m-PDA polymer

Table 3. Comparison of DSC properties of unmolded polyimide powders

Composition	Sample No.	Tg (onset), °C	Exotherm		
			Onset, °C	Peak, °C	ΔH, J/g
BTDA/BDA/m-PDA	43-54	226	365	389	29
	43-83	223	376	397	38
	43-83 from cresol	Poor definition of event	370	396	3
	Reheat of cresol sample	217	None	None	None
BTDA/HDA	78-134	134	308	336	22
	(reheat)	123	None	None	None
BTDA/HDA/m-PDA	338-85	161	342	367	22
	(reheat)	192	None	None	None
	43-50	201	342	364	39
BTDA/ODA	338-438	110	320	349	57
	(reheat)	106	None	None	None
BTDA/ODA/m-PDA (50/50 wt pct)	65-107	190	342	361	32
BTDA/BAC/m-PDA	43-69	241	336	362	65
	from cresol	None	None	None	None

temperature as the polymer isolated by heating the cresol solution for 1 hr at 250°C.

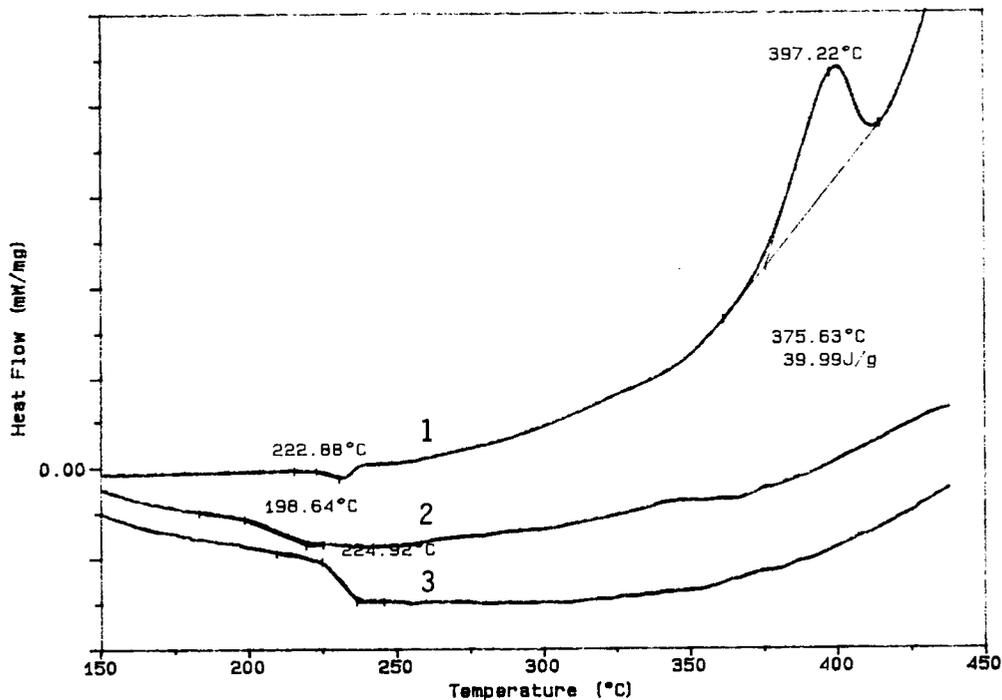
The peak exotherm temperature and ΔH values were determined for a series of varying molecular weight BTDA/HDA/m-PDA polymers. The details of this study are presented in Table 4. The peak exotherm temperatures show essentially no variation with molecular weight and the ΔH values show only a slight increase with molecular weight. All of the samples were initially isolated individually from cresol at room temperature with methyl alcohol. They were then treated for the same time with fresh methyl alcohol at 60°C, and finally vacuum dried together overnight at 200°C and 0.1 mm Hg. It can be tentatively concluded from this study that the DSC exotherm is a basic property of the polymer when isolated as fibers from the cresol reaction medium. How it varies with method of isolation, trace cresol, crosslinking, branching, and/or other possible variables is not known.

Another phenomenon was observed with the BTDA/BDA/m-PDA polymer which was not observed from BTDA/HDA/m-PDA or BTDA/BAC/m-PDA polymers. DSC analysis of the fused portion of the test disks molded at 252°, 280°, and 303°C with no hold time gave a Tg which was about 20°C lower than the unfused or unmelted portion of the disk. Reheating the DSC specimens which had once been heated to 425°C gave a final Tg for the polymer which was essentially the same as the as-prepared and unfused polymers. This behavior was repeated several times and is shown in Figure 7, which shows the DSC curves of the as-prepared polymer, the polymer after fusion for 30 min at 280°C, and the latter polymer reheated after the first DSC analysis. The fused portion of the BTDA/BDA/m-PDA polymer, which was held for 30 min at 303°C at atmospheric pressure followed by application of 6.9 MPa pressure for 30 min, gave a Tg onset temperature at 220°C suggesting that thermal history influences the Tg.

Table 4. DSC data for varying molecular weight BTDA/HDA/m-PDA polymers

Sample Number	Polymer Data				DSC Data						
	Reaction Time At 18°C (hr)	Reaction Solids Content (%)	Inherent Viscosity, dl/g (cresol)	Sample Appearance	First Heat Up		Exotherm			Reheat of DSC sample	
					Tg (°C)		Peak Temperature (°C)	ΔH (J/g)	Tg (°C)		
					Onset	Midpoint			Onset		Midpoint
43-32I	2	4.0	0.30	Powder	181	188	None	None	192	199	
43-32H	2	6.7	0.37	Fibers	193	196	364	19.7	186	192	
43-32J	2	10.0	0.67	Fibers	192	198	363	18.0	186	193	
43-32G	2	15.0	0.96	Fibers	197	202	364	24.9	191	198	
43-32Fa	2	20.0	---	Fibers	200	204	362	24.6	189	197	
43-32G	20	15.0	1.42	Fibers	202	205	361	27.0	189	195	

^aSample had opacity



Curves from top to bottom are:

Curve 1 = As prepared fibrous material

Curve 2 = Fused portion of 30 min at 280°C,
6.9 MPa processed disk

Curve 3 = Reheat of sample which gave Curve 2

T_gs shown are onset temperatures

Figure 7. DSC curves of BTDA/BDA/m-PDA polymer

3.1.3 Annealing Studies

Prior efforts showed that the room temperature and elevated temperature Barcol hardnesses of several polymers were increased with 24-hr treatment at 140°C. For example, the hardness of the BTDA/HDA/m-PDA polymer increased from 32 to 38 at room temperature with this treatment.

Small moldings of all three candidates when treated at or above their Tgs expanded in the z or mold plunger direction with concurrent shrinkage in the xy directions. Furthermore, a molding of the BTDA/HDA/m-PDA polymer was intentionally reduced in thickness from 2.31 to 1.71 mm with a corresponding increase in its area by treating it for 6 hr at 222°C under 0.4 MPa pressure and cooling under that pressure. With a single heat treatment to 300°C, the polymer cube essentially returned to its original dimensions.

The three candidate polymers were then heat treated for 16 hr at 20°, 30°, and 50°C below their Tgs. Barcol hardness measurements were made on the samples at room temperature, 93° and 140°C and a second time at room temperature at the end of the elevated temperature tests. These measurements are presented in Table 5.

Only minor benefits to the hardness of the majority of the samples are observed from various heat treatments shown in Table 5. The BTDA/HDA/m-PDA polymer shows slight improvement over the as-molded values with the 16-hr heat treatments at 20° and 30°C below Tg (176 and 166°C, respectively). The increase in hardness at 93°C with different polymer compositions is important. The BTDA/BAC/m-PDA polymer with its hardness of 45 at 93°C and 38 at 140°C shows excellent retention of the room temperature value. It is nearly twice the value of the control sample at 140°C.

Table 5. Barcol hardness of candidate polymers

Composition	Heat Treatment Temperature ^a (°C)	Test Temperature			
		Room Temperature		93°C	140°C
		Start	End		
BTDA/BDA/m-PDA	None	45	48	38	30
	202	48	48	41	35
	192	46	42	40	34
	172	46	44	40	31
BTDA/HDA/m-PDA	None	37	39	30	20
	176	44	43	35	29
	166	45	45	35	29
	146	36	41	27	23
Control ^b	N/A	42	45	35	20
BTDA/BAC/m-PDA	None	50	49	42	38
	221	49	50	46	35
	211	50	51	45	39
	191	50	50	45	38

^aSamples dried for 2 hr at 120°C and cooled in a dessicator prior to starting experiment. Samples treated 16 hr at the indicated temperature.

^bControl sample was reported in NASA CR 172568. Heat-treated sample previously gave a value of 38 at room temperature and 18 at 140°C.

Other variables associated with the specimens during heat treatment were measured and are listed in Table 6. All samples lost weight with heat treatment which was usually accompanied by a reduction in the sample's volume. The volumes of the BTDA/HDA/m-PDA polymer samples after the 146° and 166°C treatments were not reduced. The slight thickness increase observed with heat treatment is probably related to dimension changes observed when the polymers are heat treated above their T_g, as previously discussed. Thickness increase is clearly associated with shrinkage in other sample dimensions to give the observed reduction in volume. All of the moldings were heat treated for 16 hr at 30°C below the T_g of polymer.

3.1.4 Testing

The three candidate polyimides were tested for the compressive properties, fracture energies, susceptibility to moisture (water boil) and stressed solvent resistance. These tests, which are described below, were conducted on moldings prepared and annealed as described in the previous section.

Compression Properties

Moldings of the three candidate polymers were sent to Delsen Testing Laboratories, Inc., Glendale, California, for specimen preparation and compression properties determination per ASTM D695-85. Nine specimens were obtained from each molding for three replicates per test condition. The compression properties of the three candidates were obtained at room temperature, 93°C, and 93°C after 24-hr water boil. A summary of the test results is provided in Table 7. Table 7 also gives the percent moisture weight gain after 24-hour water-boiled specimens.

The compression properties obtained by extensometer on the three candidates suggest good potential as composite matrices. The BTDA/BAC/m-PDA

Table 6. Physical property changes of heat treated specimens

Composition	Heat Treatment Temperature ^a (°C)	Thickness Increase (%)	Weight Loss (%)	Volume Change (%)	Specific Gravity of Heat-Treated Specimen (g/cc)
BTDA/BDA/m-PDA	202	0.2	0.30	-0.22	1.3807
	192	0.1	0.31	-0.19	1.3808
	172	None	0.30	-0.12	1.3791
BTDA/HDA/m-PDA	176	0.1	0.21	-0.17	1.3609
	166	0.1	0.19	+0.04	1.3584
	146	0.1	0.15	+0.02	1.3596
BTDA/BAC/m-PDA	221	0.1	0.34	-0.37	1.3377
	211	0.2	0.33	-0.34	1.3370
	191	0.2	0.32	-0.18	1.3359

Table 7. Summary of average compression test results on the three candidate polymers

Composition	Compressive Properties											
	Stress at Proportional Limit, MPa (psi)			Stress at Yield, MPa (psi)			Modulus, GPa (psi X 10 ⁵)			Strain at Yield (%)		
	RT	93°C DRY	93°C MET	RT	93°C DRY	93°C MET	RT	93°C DRY	93°C MET	RT	93°C DRY	93°C MET
BTDA/BDA/m-PDA	86.1 (12,500)	56.9 (8,260)	54.3 (7,880)	221 (32,000)	152 (22,000)	145 (21,000)	4.37 (6.34)	3.48 (5.05)	3.45 (5.00)	8.56	7.51	7.43
BTDA/HDA/m-PDA	76.5 (11,100)	36.1 (5,240)	42.1 (6,100)	199 (28,700)	132 (19,100)	125 (18,200)	3.92 (5.69)	3.54 (5.14)	3.39 (4.92)	8.75	6.71	6.54
BTDA/BAC/m-PDA	67.6 (9,810)	62.8 (9,110)	55.4 (8,040)	223 (32,300)	161 (23,300)	154 (22,400)	4.85 (7.04)	3.67 (5.33)	3.81 (5.54)	8.59	7.38	7.20

Note: 93°C wet are 24-hr water-boiled specimens

Water Absorption (Weight Gain)	
Composition	Weight Gain (%)
BTDA/BDA/m-PDA	0.65
BTDA/HDA/m-PDA	0.56
BTDA/BAC/m-PDA	0.68

polymer had a modulus at room temperature of 4.85 GPa, the BTDA/HDA/m-PDA polymer a modulus of 3.92 GPa, and the BTDA/BDA/m-PDA polymer a modulus of 4.37 GPa. These compression moduli values are higher than familiar engineering thermoplastics cited in the 1986-87 Modern Plastics Encyclopedia. For example, polyamide-imide is seen to have a compression modulus of 1.9-3.1 GPa, polyetherimide a modulus of 2.9 GPa, and polysulfone a modulus of 2.7 GPa. The high compression moduli of the program polymers is consistent with expectation and with the Barcol hardness values discussed in the previous sections.

Stress at proportional limit (end of Hookean elasticity) is excellent for all three polymers at room temperature. This value would be expected to be important in predicting compression fatigue properties of the candidate resins. The proportional limit stress of the BTDA/BAC/m-PDA polymer is somewhat lower than the other two polymers at room temperature but is clearly superior at 93°C.

Previous² compression properties determination by strain gage on the BTDA/HDA/m-PDA polymer by Acurex are consistent with the room temperature values reported by Delsen. However, the compression yield strength of 132 MPa for the BTDA/HDA/m-PDA polymer at 93°C is much higher than the 100 MPa value measured previously at 82°C on this polymer. An increase in elevated temperature Barcol hardness is also observed for the composition tested in Table 7 over previously measured values. (See Table 1, entries 8 and 8A.)

Tensile Properties

Quality moldings were not prepared from the three candidates as planned, because of their marginal flow properties. Due to schedule constraints, polymer selection was made without these values. Because of their high inherent viscosities (~1.0 dl/gm), it is expected that all three

polymers, if completely molded, would have tensile properties equal to or better than those previously² determined for the BTDA/HDA/m-PDA polymer.

Fracture Toughness Properties

Moldings sent to NASA-Langley were sectioned and K_{IC} values determined for specimens in the as-molded condition as well as specimens given the annealing schedule previously described. These values are given in Table 8. G_{IC} was estimated from compression moduli results given in Table 7 and an assumed Poisson's ratio of 0.35 for all three polymers.

The three polymers show a slight increase in K_{IC} and G_{IC} values with increasing T_g and decreasing linear aliphatic weight percent content. This trend is opposite to expectation. Relevant to program goals, the values are acceptable.

Dry- and Water-Boiled Properties

The three polymers were subjected to thermal mechanical analysis (TMA) for T_g determination and T_g shift due to moisture exposure. Expansion measurements were used for dry T_g determination and failure temperature under compression load (FTUCL). (See Appendix A for the effect of moisture on 24-hr water-boiled specimens.) These results are presented in Table 9 with inherent viscosity, Barcol hardness, and 50-day chloroform weight-gain values. The samples had nominal dimensions of 0.2 cm X 0.6 cm X 0.6 cm.

Expansion coefficient determination on the polymers by TMA was not straightforward. Heating the as-molded annealed samples the first time lead to shrinkage in the xy dimensions with a corresponding growth in the thickness or z dimension. The cooling curve was not superimposable on the heating curve. Several reheats of the same specimen were required to obtain near superposition of the heating and cooling curves and to bring the glassy

Table 8. Fracture energies of the three candidate polymers

Composition	K_{Ic}^a MPa \sqrt{m} (psi \sqrt{in})	G_{Ic}^b J/m ² (in-lb/in ²)
BTDA/BDA/m-PDA		
As molded	2.43 (2220)	1193 (7.8)
Heat treated 16 hr at 192°C	2.43 (2220)	1193 (7.8)
BTDA/HDA/m-PDA		
As molded	2.16 (1970)	1044 (6.8), (8.1) ^c
Heat treated 16 hr at 166°C	2.12 (1930)	1002 (6.5)
BTDA/BAC/m-PDA		
As molded	2.72 (2480)	1337 (8.7)
Heat treated 16 hr at 211°C	2.78 (2540)	1403 (9.2)

^a Compact tension prepared and tested by NASA Langley Research Center

^b Values calculated using compression moduli from Table 7 using $G_{Ic} = K_{Ic}^2/E(1-\nu^2)$

^c Value calculated from tensile modulus obtained on prior program (485,000 psi)²

Table 9. Dry- and water-boiled properties of the three candidate polymers

Composition	Inherent Viscosity, dl/gm (cresol)	Dry Properties				24-hr Water-Boiled Properties			50-Day Chloroform Weight Gain (%)
		Barcol Hardness	Tg °C	FTUCL, °Ca		FTUCL, °Ca Intercept	Weight Gain (%)		
				Deviation From Linearity	Intercept				
BTDA/BDA/m-PDA	1.05	46	223	170	215	184	1.6	1.5	
BTDA/HDA/m-PDA	0.90	41	196	145	191	163	1.8	4.8	
BTDA/BAC/m-PDA	0.90	50	241	185	236	203	1.7	1.5	

aFTUCL = failure temperature under compression load

expansion coefficient near the T_g to about 1/3 of the value for the melt expansion coefficient.

Figure 8 provides an example of the behavior of the BTDA/BAC/m-PDA polymer on the first and fifth heating and cooling cycles. The polymer lost 1.1 percent of its weight during the first three cycles and 1.2 percent of its thickness. It lost essentially no weight or thickness during the fourth and fifth cycles. Similar behavior was observed for both the BTDA/BDA/m-PDA and BTDA/HDA/m-PDA polymers. Figure 9 provides the last heating cycles for these polymers. T_g 's were obtained from the intercept of the glassy and melt curves. Expansion coefficients are given in the figures.

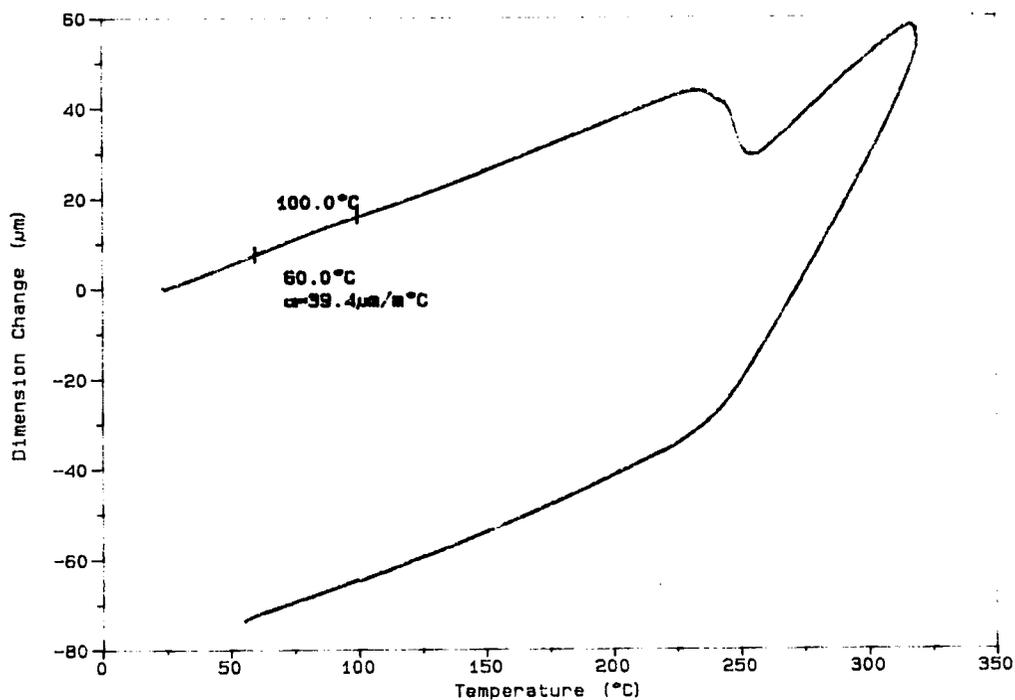
FTUCL temperatures under the 0.3 MPa (450 psi) load were determined on dry and 24-hr water-boiled samples. The shift, due to water boil, in all three polymers is about 30°C. The weight gains for the three polymers is between 1.6 and 1.8 percent which is about a factor of 3 less than values obtained with epoxy resin based on MY720.³

Fifty-day chloroform absorption values are also provided in Table 9. The BTDA/HDA/m-PDA polymer which showed a weight gain of 4.8 percent is slightly lower than previously observed; however, 1-hr heat treatments at 316°C reduced these previous values to about 2 percent weight gain. Both the BTDA/BDA/m-PDA and BTDA/BAC/m-PDA polymers show about a three-fold improvement over the BTDA/HDA/m-PDA polymer in Table 9 with weight gains of 1.5 percent. The values provided in Table 9 suggest adequate performance for all three polymers relevant to the 93°C wet performance sought in the program.

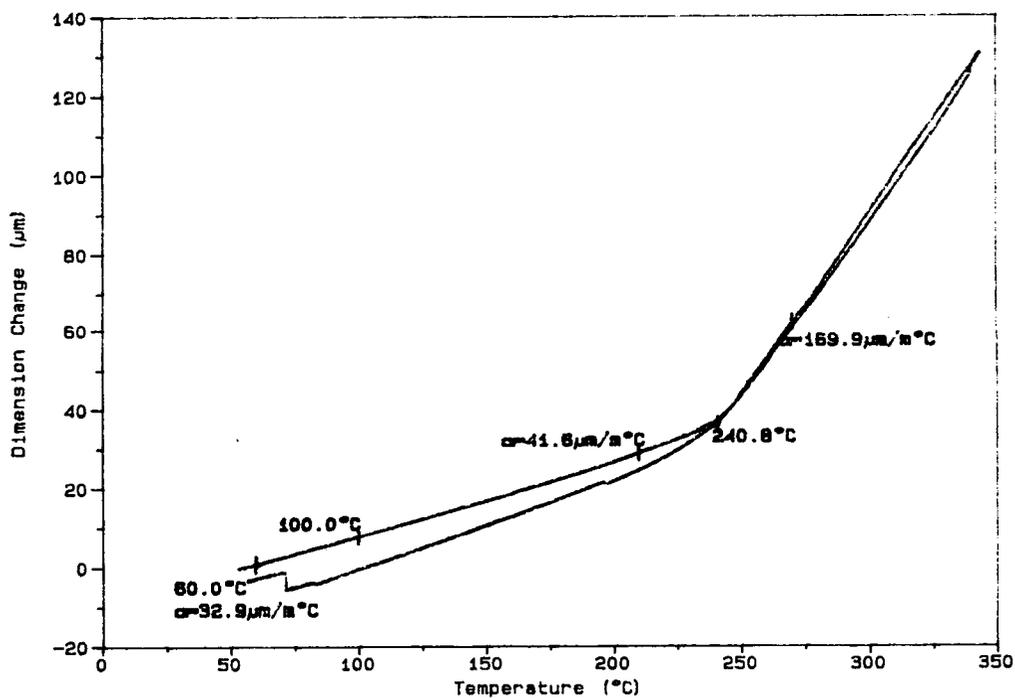
Stressed Solvent Resistance Properties

The three candidates were immersed in deicing fluid, hydraulic fluid, and two paint strippers under stress. The stressed condition was achieved with a small flexural specimen which was clamped in a three-point bend fixture

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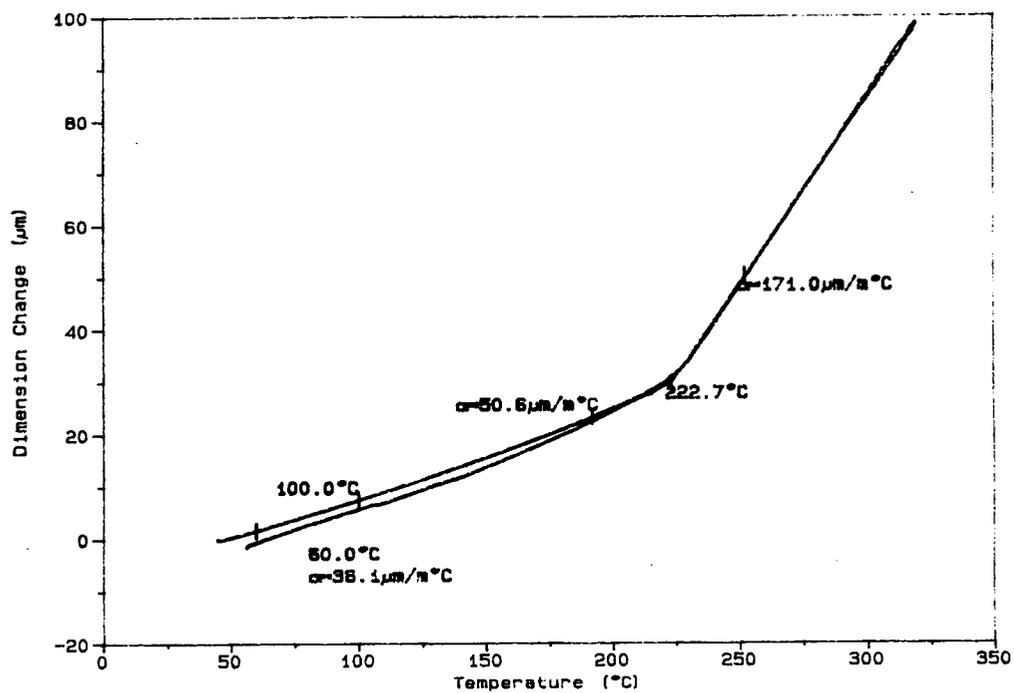


(a) BTDA/BAC/m-PDA -- first cycle

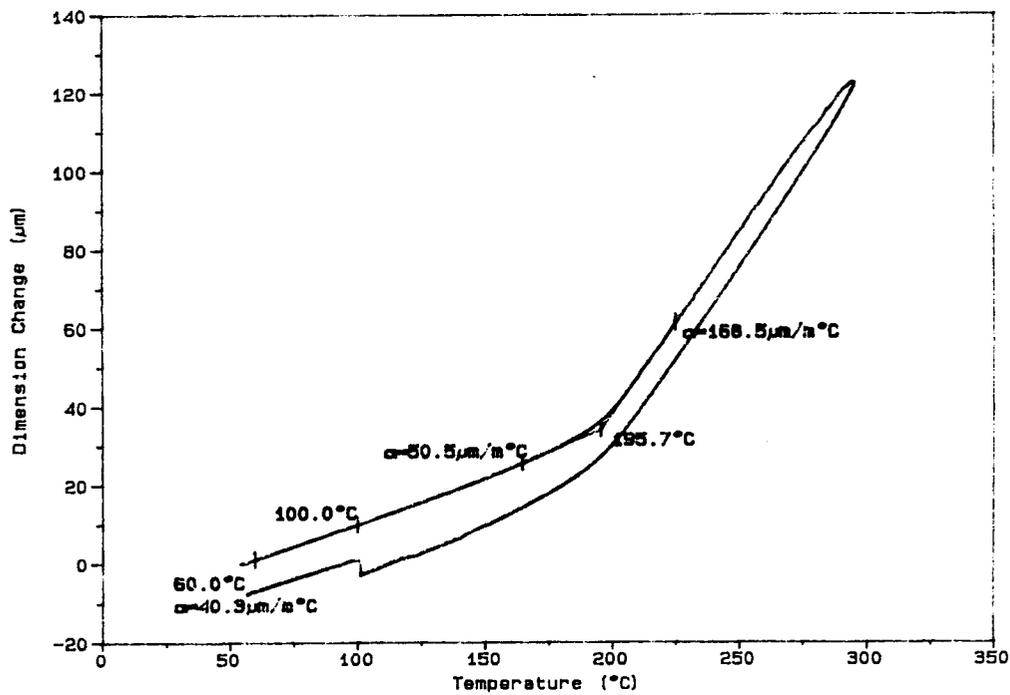


(b) BTDA/BAC/m-PDA -- fifth cycle

Figure 8. TMA curves for BTDA/BAC/m-PDA polymer



(a) BTDA/BDA/m-PDA



(b) BTDA/HDA/m-PDA

Figure 9. TMA curves for BTDA/BDA/m-PDA and BTDA/HDA/m-PDA polymers

to a 0.127 cm (0.047 in) deflection over a 3.81 cm (1.50 in) span. This deflection was calculated to produce a 34.5 MPa (5000 psi) tensile stress on the tensile side of the test coupon for a specimen which was 0.203 cm (0.080 in) thick with a modulus of 3.45 GPa (500,000 psi). The candidates had nominal thicknesses of 0.215 cm (0.085 in) and moduli as indicated in Table 7. Consequently, test specimen thickness and modulus variance from the design condition produced slightly higher or lower tensile stresses than the calculated 34.5 MPa (5000 psi) value.

The paint strippers were of two types: a nonacid stripper (CEE BEE A-254) and an acid stripper (Inland Chemical AP-561A). They were obtained from the United Airlines repair facility at the San Francisco airport and are in current use. Plans are to slowly convert to the acid stripper for its greater acceptability from environmental considerations (employee health, disposal, etc.). Both meet the McDonnell Douglas CSD1 and Boeing D6-17487 specifications for use on their respective aircraft. The compositions are thought to be methylene chloride-phenol and methylene chloride-formic acid. However, the latter composition, upon evaporation, has the sweet odor of phenol. The strippers are used to remove the urethane paint and the epoxy primer from aluminum. Windows and composite wing fairings are no doubt masked to prevent exposure. United Airlines currently removes paint from composites by hand sanding; however, a number of new methods are being investigated for this application, i.e., plastic media blasting.

The results of the stressed aircraft fluid and paint stripper tests are given in Table 10. All three candidates passed the 30-day exposure to hydraulic and deicing fluids based on a pass/fail criterion. All three candidates showed weight gains and did not completely return to their original

Table 10. Stressed aircraft fluid and paint stripper resistance of the three candidate polymers

Composition	16-Hr Testsa		30-Day Tests			
	Nonacid Paint Stripper Weight Gain (%)	Acid Paint Stripper Weight Gain (%)	Hydraulic Fluidb		Deicing Fluidc	
			Weight Gain (%)	Deflectiond at Test End (%)	Weight Gain (%)	Deflectiond at Test End (%)
BTDA/BDA/m-PDA	37	20	0.6	15	1.3	20
BTDA/HDA/m-PDA	106	105	0.4	10	1.0	30
BTDA/BAC/m-PDA	49	39	0.6	10	1.4	25

a All specimens failed (did not support any load) within 16 hr.

b No deflection was recovered on removal of the load.

c Mansanto's fire-resistant hydraulic fluid Skydrol® 500B

d 50-50 ethylene glycol-water mixture

e Flexural specimens were deflected for exposure to test liquid, deflection measured at end of test is expressed as a percentage of original deflection (20 percent deflection is 80 percent recovery of the original deflection)

original flat condition. The 7-day recovery deflections of all specimens shows less than 0.0012 cm (0.005 in) or 10 percent permanent deflection.

Exposure to both paint strippers led to failure of all three candidates in less than 16 hr. This result was unexpected, due to the excellent chloroform resistance of the candidates. It is likely due to the combined solvent effects of phenol or formic acid with the methylene chloride.

This result prompted collection of polymer samples from a number of compositions for test in the two paint strippers. Since these samples had varying weights, percent weight gains only indicate resistance or attack and do not allow for a comparison between compositions. The three polymers tested in the stressed-solvent tests described above were all close to the same dimensions.

Results of the tests on the collected samples are given in Table 11. The best compositions are either crystalline or crosslinked. One composition showed no weight gain in the 16-hr tests. It was a highly crosslinked novolac cyanate (NC) resin.⁴ Tests were continued for 12 days for samples which showed no surface attack by the paint strippers in the 16-hr tests. The 12-day exposed samples were then allowed to stand out under ambient conditions to see if they would return to their original weights. These data are presented in Table 12.

It is concluded that solvation differences between paint strippers exist and depend on the specific composition of the paint stripper. The 12-day exposed Kapton film results point out this difference. Samples of Kapton after 16-hr exposure in both paint strippers showed weight gains of about 30 percent and no surface attack. However, 12-day exposure led to liquification of the Kapton sample in the nonacid paint stripper but had no

Table 11. Sixteen-hour unstressed weight gains of various compositions in paint strippers

Composition ^a	Nonacid Paint Stripper	Acid Paint Stripper
Program Resins		
BTDA/BDA/m-PDA		
As molded, annealed	23	43
After 1 hr at 316°C	14	10
BTDA/HDA/m-PDA		
As molded, annealed	215	240
After 1 hr at 316°C	223	161
BTDA/BAC/m-PDA		
As molded, annealed	123	49
After 1 hr at 316°C	45	43
Prior program resins		
BTDA/ODA/m-PDA	61	36
PBI from TAB with sebacic acid	242	Dissolved
PMDA/ODA	4	4
Miscellaneous thermoplastics		
Kapton	32	27
Ultem	Dissolved	Dissolved
Miscellaneous thermosets		
EPON 828/NMA	51	Lost
DGA/Tonox	0	1
MY720/DDS	0.2	0.2
NC	0	0
Miscellaneous composites		
Ryton/carbon	8	11
Peek/carbon	3	4

^aODA = 1,8-octanediamine
PBI = polybenzimidazole
TAB = 3,3',4,4'-tetraaminobiphenyl
PMDA = pyromellitic dianhydride
NMA = methylnadic anhydride
DDS = 4,4'-diaminodiphenylsulfone
NC = novolac cyanate
DGA = diglycidylaniline

Table 12. Twelve-day unstressed weight gains of compositions in paint strippers

Composition ^a	Nonacid Paint Stripper	Acid Paint Stripper
	12-Day Weight Gain (%)	
BTDA/BDA/m-PDA (after 1 hr at 316°C)	193	164
PMDA/ODA	25	19
Kapton	Liquified	28
MY720/DDS	1.6	3.2
NC	0	1.1
Ryton/carbon	13	12
Peek/carbon	11	5
	Weight Gain After 2 days at Ambient Condition (%)	
BTDA/BDA/m-PDA (after 1 hr at 316°C)	82	58
PMDA/ODA	11	9
Kapton	--	10
MY720/DDS	0.7	0.7
NC	-0.7	0
Ryton/carbon	1.4	2.1
Peek/carbon	3.6	0

^aODA = 1,8-octanediamine
PBI = polybenzimidazole
TAB = 3,3',4,4'-tetraaminobiphenyl
PMDA = pyromellitic dianhydride
NMA = methylnadic anhydride
DDS = 4,4'-diaminodiphenylsulfone
NC = novolac cyanate
DGA = diglycidylaniline

further influence on the sample in the acid stripper. The term liquification means the sample lost its dimensions but did not dissolve.

Relevant to program goals, the three polymers demonstrated good resistance to hydraulic and deicing fluids and chloroform. Prior program efforts suggest that resistance to acetone will be even better than the chloroform resistance. Short time exposure (1 to 2 hr) to paint strippers which contain a combination of chlorinated and acidic solvents may be acceptable but overnight exposure must not occur.

In view of the 2-day recovery test results indicated in Table 12 which show the presence of residual paint stripper in most of the polymers, it can be concluded that paint strippers should not be used on crosslinked or crystalline polymers without prior extensive testing. Structural composites should show 100 percent recovery of properties after intentional or accidental exposure to aircraft fluids and paint strippers. Paint stripper reformulation is probably required to achieve this goal.

3.1.5 Selection

The BTDA/BDA/m-PDA and BTDA/BAC/m-PDA polymers are superior to the BTDA/HDA/m-PDA polymer in compression properties and resistance to paint stripper. The remainder of the tests show the three polymers to be about the same without clear benefit for use of one over the other two. The BTDA/BDA/m-PDA polymer is slightly more resistant to paint stripper than the BTDA/BAC/m-PDA polymer, particularly after 1-hr heat treatment at 316°C. The BTDA/BDA/m-PDA polymer is less moldable than the BTDA/BAC/m-PDA polymer. This moldability rating is subjective and based on a seemingly better ability of the BTDA/BAC/m-PDA polymer to give thin moldings than the BTDA/BDA/m-PDA polymer.

The polymers used for the characterization tests had inherent viscosities close to 1 dl/g in cresol. As demonstrated in subsequent sections of this report, the poor moldability of the three candidates at low pressure was due to their high molecular weight. Based on this premise in combination with the characterization tests, the BTDA/BAC/m-PDA polymer was recommended for the molecular-weight/melt flow optimization studies.

3.2 MOLECULAR WEIGHT/MELT FLOW OPTIMIZATION STUDIES

The objective of this effort was to increase flow properties of the selected polymer by controlling (reducing) its molecular weight. Stoichiometric imbalance (excess BTDA) and end capping with phthalic anhydride were investigated. As a point of reference which assumes complete reaction (which is not likely for second-order polymerizations), the BTDA/BAC/m-PDA polymer with a 10,200 MW would result from an amine stoichiometry of 96.0 percent (DP = 49) and a polymer with a 20,400 MW would result from an amine stoichiometry of 98.0 percent (DP = 99).

The polymer from BTDA with BAC and m-PDA was selected for investigation with NASA's verbal approval obtained on 7/9/86. Molecular-weight tailoring efforts demonstrated that the BTDA/BAC/m-PDA polymer had very limited potential to provide low-molecular-weight polymers with the desired flow properties. When a methyl group is placed ortho to one or both of the amine groups in the m-PDA, the resulting polymers were produced in both low and high molecular weights with flow properties as expected. Telecom with the NASA technical representative on 12/1/86 lead to verbal approval to proceed with substitution of the m-PDA in the BTDA/BAC/m-PDA polymer with 2,4-diaminotoluene (2,4-DAT). The balance of work in the program was carried out with the BTDA/BAC/2,4-DAT polyimide.

3.2.1 Flow Properties

Optimizing the flow properties of the selected polymer required a flow test be used to monitor progress of these efforts. Three tests were conducted on the different molecular-weight levels of the polymer investigated.

Molding Tests

This test was described in Section 3.1.2. For the molecular-weight tailoring efforts, the pressure was reduced from 6.9 MPa (1000 psi) to 1.45 MPa (210 psi). The 5.07 cm² (1 in²) mold was loaded with 0.5g fibrous polymers at a 45° angle as previously described. Completely molded specimens would have an areal weight of 0.1 g/cm². All tests were conducted for 30 min at 303°C.

TMA Flow Test

The developed TMA flow test is a penetration test wherein a sample is placed under a weighted probe and subsequently heated. The resulting curves are normalized to 100 percent penetration to allow samples of varying thicknesses to be compared. Further description of this technique is provided in Appendix B. Unless otherwise noted, flow curves given in this section of the report were conducted at 0.20 MPa (28 psi).

Press Flow Test

Acurex compares the melt flow properties of resins by placing a weighed sample in a press equipped with an accumulator which applies a constant force to the sample. The area of the resulting disk obtained after a prescribed time is related to the melt viscosity of the polymer. The procedure is calibratable. Figure 10 shows the areas of 0.5g disks of polysulfone (UDEL P1700) and polyetherimide (ULTEM P1000) pressed for 5 min with 95 Kg (210 lb) force at the indicated temperatures. Inherent viscosities of the two polymers

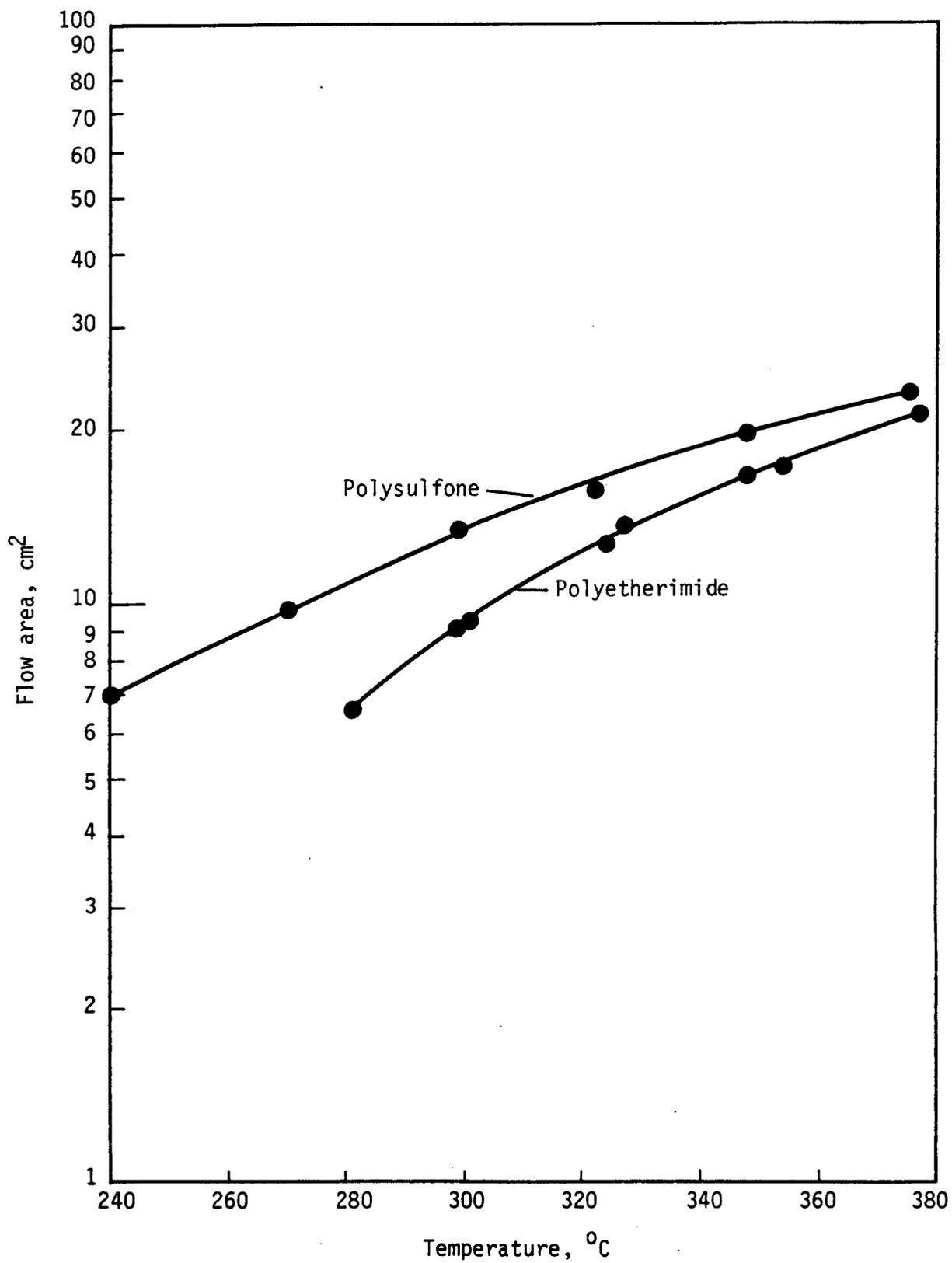


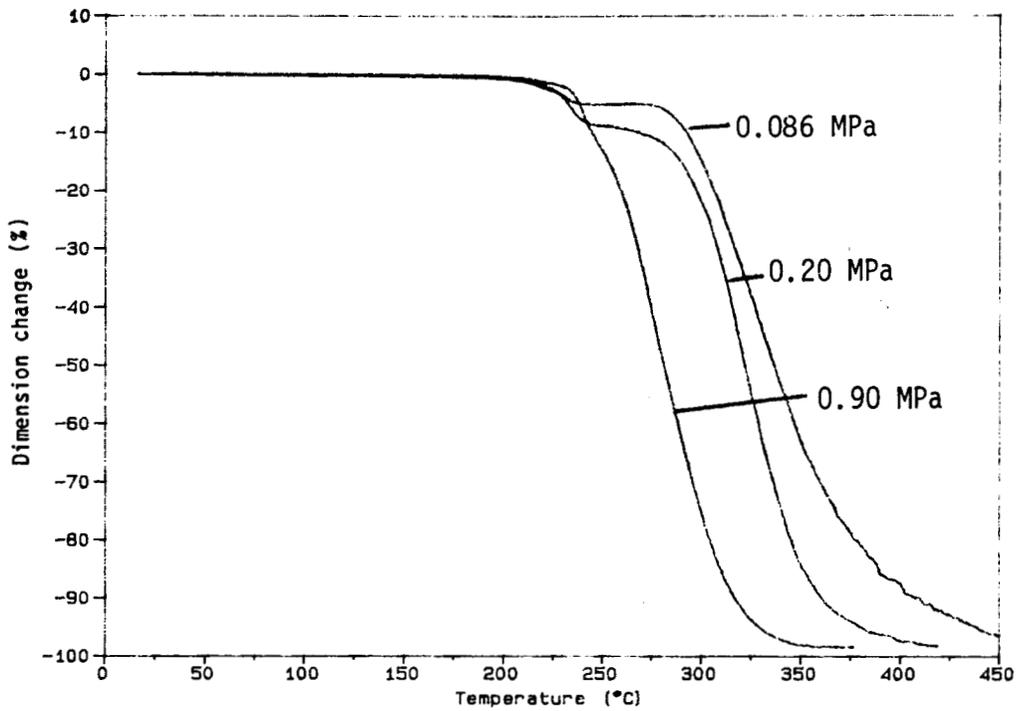
Figure 10. Press flow areas of polysulfone and polyetherimide

in cresol were 0.488 and 0.543 dl/g, respectively. The Tg's of the polymers were 187° and 217°C, respectively (DSC inflection points).

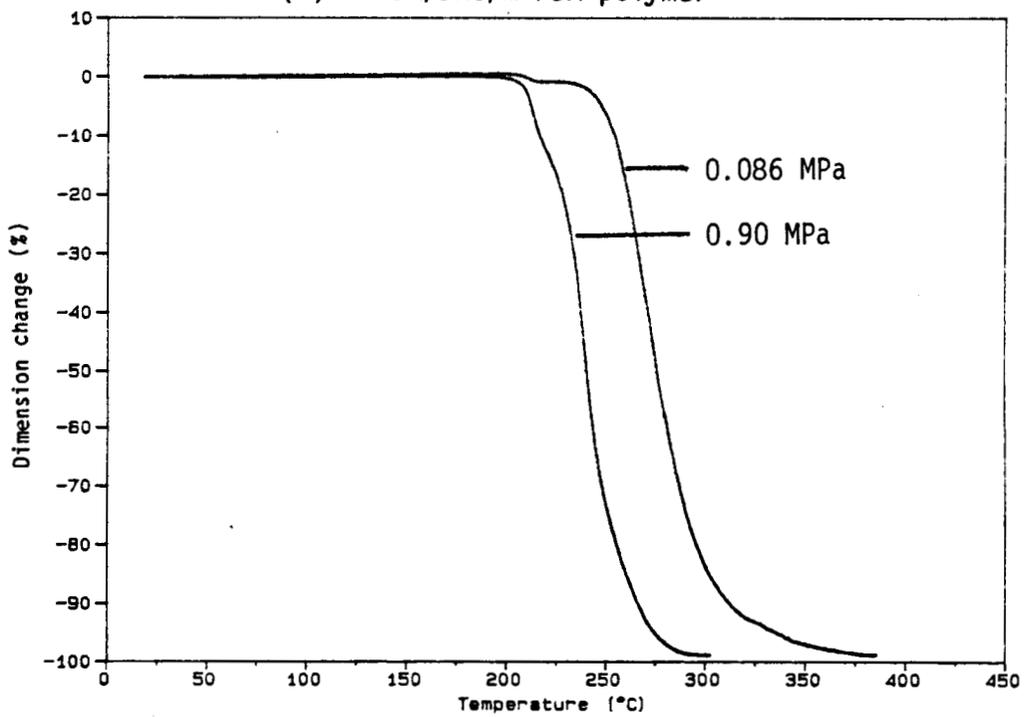
3.2.2 BTDA/BAC/m-PDA Polymer

Experiments with both phthalic anhydride end-capped and imbalanced stoichiometry were carried out on the title polymer. With both approaches, at stoichiometries of less than 99.0 percent, opacity developed during the polymerizations. The degree of opacity is directly related to the stoichiometry. That is, reactions with only 95 percent of the amine have more opacity than higher amine percentages. Brief treatment of the opaque polymers at 429°C resulted in volatile loss (foaming) and a clear polymer. Opacity was eventually traced to the "crystalline" nature of the intermediates formed. This is discussed in some detail in Appendix C and summarized below.

End-capping experiments with phthalic anhydride (PA) at 97.5 percent BTDA stoichiometry (BTDA = 0.975 mole, amines = 1.000 mole, PA = 0.050 mole) lead to only one polymer with excellent flow properties. The flow properties of this polymer are compared to the flow properties of polyetherimide in Figure 11. Flow pressures used for the three flow curves for the BTDA/BAC/m-PDA polymer were 0.086 MPa (12.5 psi), 0.20 MPa (28 psi), and 0.90 MPa (130 psi). For the polyetherimide, only the 0.086 MPa and 0.90 MPa pressures were used. Although the BTDA/BAC/m-PDA polymer was somewhat brittle, its flow properties were consistent with program goals: a polymer which flowed at low pressure. The flow properties of this polymer were in distinct contrast to other 97.5 percent stoichiometric compositions described in Appendix C and the 100 percent stoichiometric composition described in Appendix B. The polymer with the desired flow properties was isolated from a clear cresol solution by quenching in methanol.



(a) BTDA/BAC/m-PDA polymer



(b) Polyetherimide

Figure 11. Comparison of the flow properties of the BTDA/BAC/m-PDA polymer to polyetherimide

Polymers isolated by evaporation of the cresol exhibit an endotherm at about 350°C and flow properties representing the presence of crystallinity. It was known that this behavior is attributable to the BTDA/m-PDA/BTDA segments in the polymer since the BTDA/BAC polymer did not exhibit a high-temperature endotherm. The program approach dictated that good flow properties must be exhibited by the polymer after evaporation of a suitable prepregging solvent.

Consequently, the synthesis of clear polymers which did not have a high-temperature endotherm were required before the molecular weight/melt flow properties would be optimum. Efforts then focused on this aspect of the end-capping efforts.

It was found that when BTDA is condensed with an aromatic diamine at a 2 to 1 stoichiometry at 15 percent solids in cresol, both crystalline and amorphous adducts can be obtained. When the aromatic diamine is m-PDA, a precipitate is formed after only a few minutes reaction at 180°C. With 4,4'-methylenedianiline, a clear solution is obtained; however, upon cresol evaporation, an opaque solid is obtained. When either 2,6- or 2,4-diaminotoluene is condensed with the BTDA, evaporation of the cresol at 180°C from the clear solution leads to clear amorphous adducts.

A 96 percent amine stoichiometric BTDA/BAC/2,4-DAT polymer was clear upon evaporation of the cresol from the reaction mixture. In addition, the 1-hr at 329°C treated sample showed no high-temperature endotherm.

3.2.3 BTDA/BAC/2,4-DAT Polymers

Clear, amorphous BTDA/BAC/2,4-DAT polymers were obtained from 90, 96, 97, 97.5, 98, 98.5, and 100 percent stoichiometries. TMA flow curves, IVs, and other properties of these polymers, as well as blends of selected polymers, are provided in Figures 12 and 13 and Tables 13 and 14. TMA flow

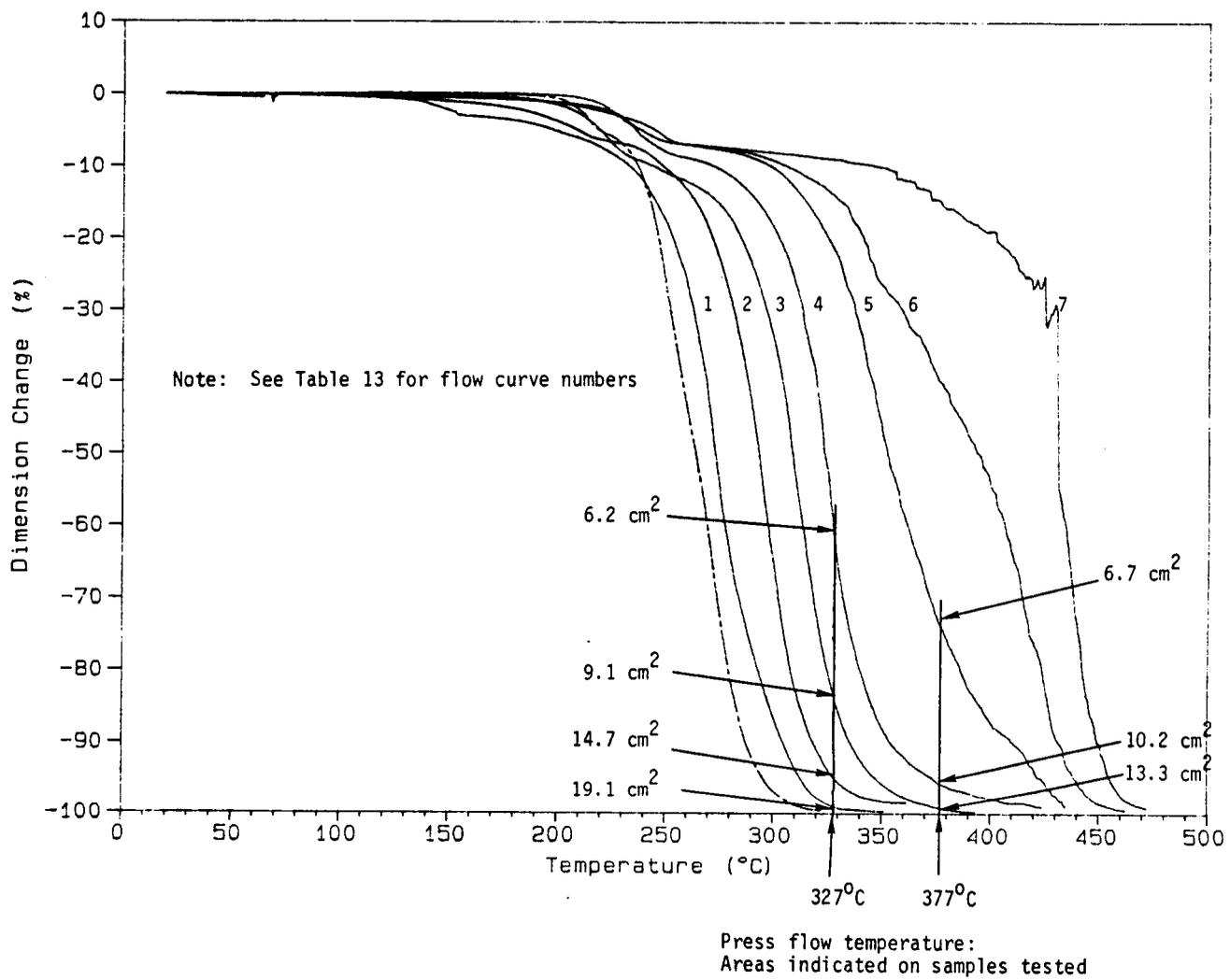


Figure 12. TMA flow curves of BTDA/BAC/2,4-DAT polymers

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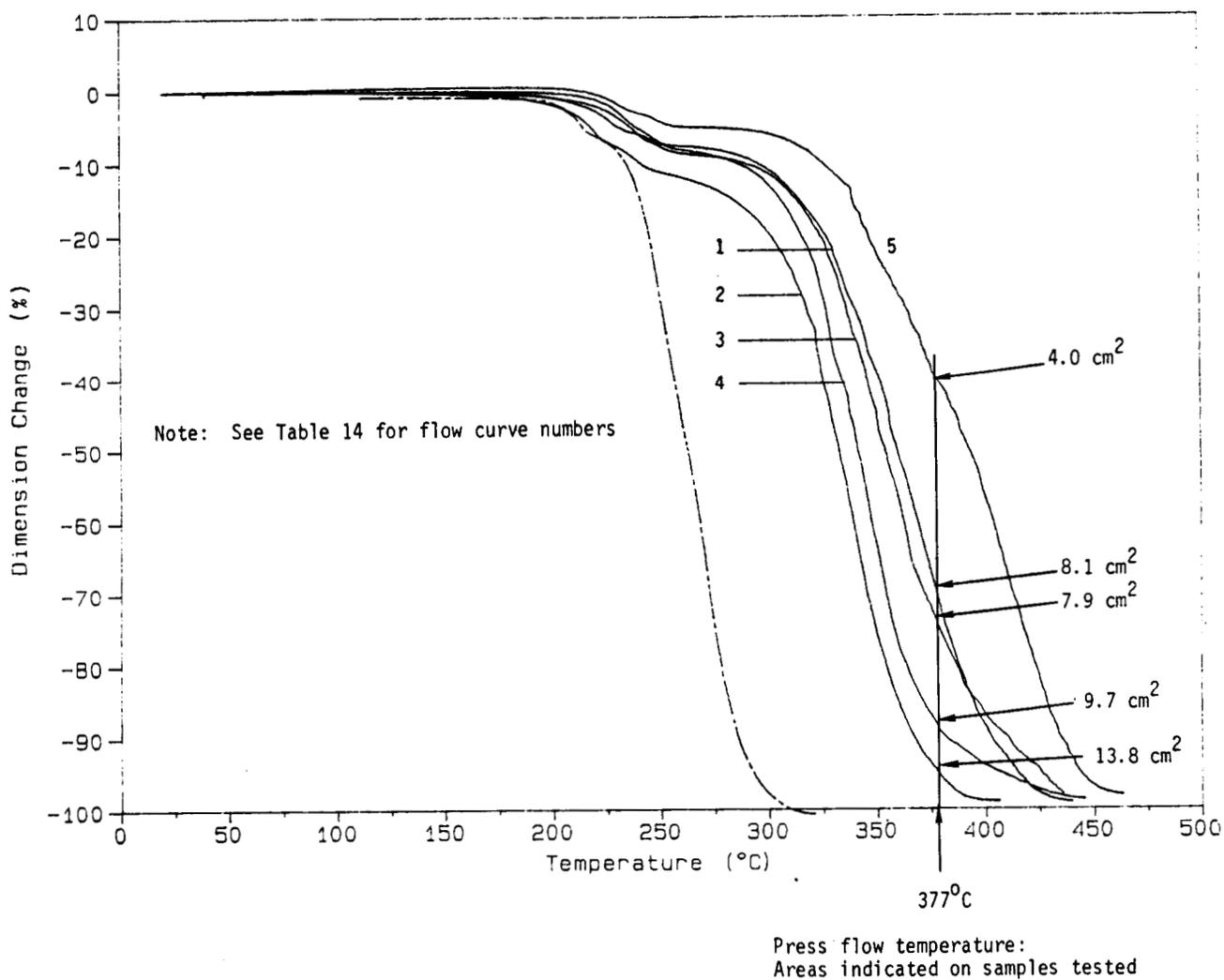


Figure 13. TMA flow curves of BTDA/BAC/2,4-DAT polymer blends

Table 13. Properties of varying molecular weight BTDA/BAC/2,4-DAT polymers

Table Number	Stoichiometry of Sample (%)	Brookfield Viscosity ^a (Pa.s)	Tg (°C)		Inherent Viscosity (dl/g)	Percent Molded	TMA 50% Flow Temperature (°C)	Press Flow Area (cm ²)	
			Onset	Midpoint				327°C	377°C
1	96	0.95	229	238	0.306	100	273	19.10	30.10
2	97	1.39	219	237	0.336	98	292	14.69	27.51
3	98	2.71	226	242	0.436	95	308	9.07	13.33
4	98.5	3.92	236	243	0.501	80	322	6.23	10.18
5	99	7.84	240	248	0.590	70	353	--	6.74
6	99.5	18.40	234	244	0.735	60	393	--	4.00
7	100	84.00	213	232 ^b	1.028	95 ^b	--	--	--

^a15 percent solids reaction mixture at 25°C

^bSample probably contained cresol contaminate

Table 14. Properties of BTDA/BAC/2,4-DAT polymer blends

Table Number	Blend Composition ^a	T _g (°C)		Inherent Viscosity (dl/g)	Percent Molded	TMA 50% Flow Temperature (°C)	Press Flow Area (cm ²)	
		Onset	Midpoint				377°C	
1	15% of 75 with 85% of 99.2 polymers	237	244	0.633	75	361	8.11	
2	30% of 75 with 70% of 99.2 polymers	228	236	0.543	80	335	13.78	
3	15% of 96 with 85% of 99.2 polymers	237	246	0.649	65	358	7.90	
4	30% of 96 with 70% of 99.2 polymers	231	245	0.549	65	341	9.68	
5	100% of 99.2 polymers	248	254	0.735	65	391	4.00	

^aInherent viscosities of 75 and 96 percent stoichiometry polymers were 0.127 and 0.321, respectively

curves, IVs, and other properties of the BTDA/HDA/2,4-DAT polymers are given in Figure 14 and Table 15. Press flow areas determined at 327 and 377°C are indicated in some of the figures. For a reference point in each of the three figures, the TMA flow curve of polyetherimide has been included (dashed line). Figure 15 provides a plot of the inherent viscosities of different molecular weight levels and polymer blends of the BTDA/BAC/2,4-DAT and the BTDA/HDA/2,4-DAT polymer. The relationship indicated in Figure 15 shows that the inherent viscosities of the BTDA/BAC/2,4-DAT polymers are directly related to the polymer's flow properties as measured by the TMA flow test at 0.20 MPa (28 psi) pressure. A one-tenth increase in inherent viscosity value leads to about a 30°C increase in the 50 percent flow temperature. Normalizing the 50 percent flow temperature by subtracting the Tg from the 50 percent flow temperature provides the results given in Figure 16. The normalized data for the two polymers show that Tg values essentially account for the differences observed in the 50 percent flow temperatures for the two compositions in Figure 15. Thus, for a given inherent viscosity polymer, the 50 percent TMA flow temperature can be estimated if the polymers' Tg is known.

The normalized values for polysulfone, polyetherimide, and blends of BTDA/2,4-DAT/BAC and HDA polymers have been added to Figure 16. The 50 percent TMA flow temperatures for these polymers is less than 50°C above their Tgs but should be about 90°C above their Tgs to fit within the data for the BTDA/2,4-DAT/aliphatic diamine polymers.

The press flow method of characterizing the flow properties of the polymers shows that polysulfone and polyetherimide are approximately equal to the flow properties of the BTDA/HDA/2,4-DAT polymers. Flow properties obtained at 327° and 377°C are plotted against inherent viscosities in

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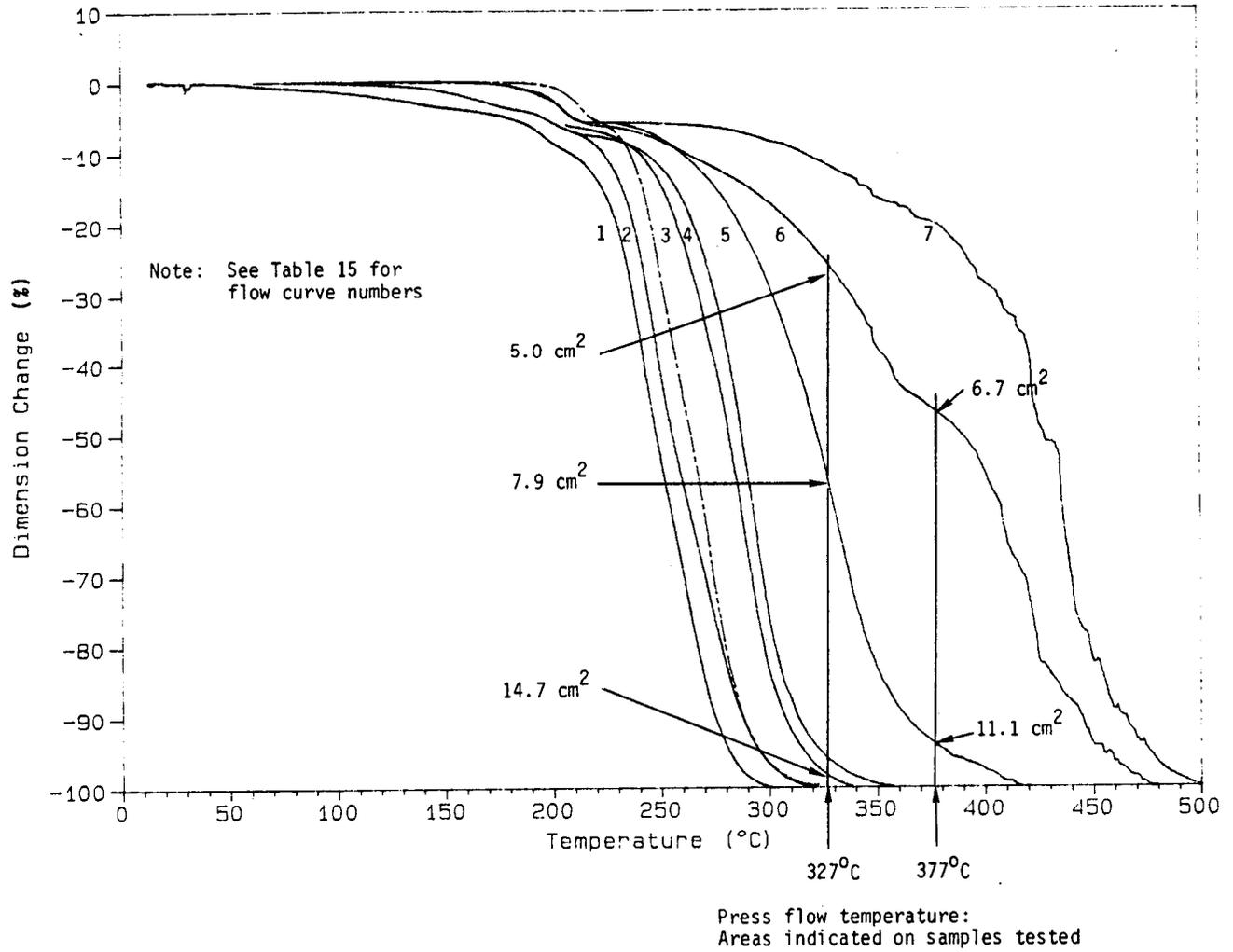


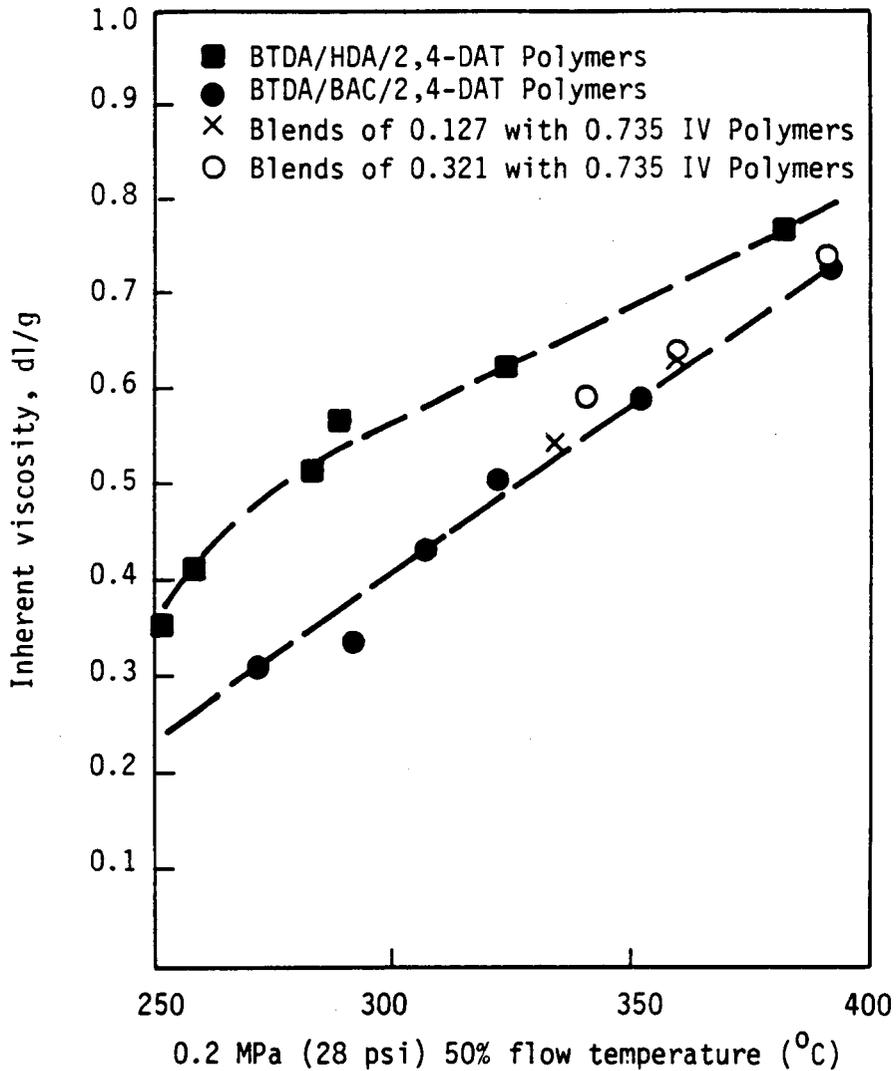
Figure 14. TMA flow curves of BTDA/HDA/2,4-DAT polymers

Table 15. Properties of various molecular weight BTDA/HDA/2,4-DAT polymers

Table Number	Stoichiometry of Sample (%)	Brookfield Viscosity ^a (Pa·s)	Tg (°C)		Inherent Viscosity (dl/g)	Percent Molded	TMA 50% Flow Temperature (°C)	Press Flow Area (cm ²)	
			Onset	Midpoint				327°C	377°C
1	95	1.33	190	196	0.365	100	251	--	--
2	96	2.34	193	200	0.417	100	257	21.43	32.33
3	97	3.63	199	206	0.518	100	284	14.69	21.03
4	97.5 ^b	3.22	199	207	0.575	100	290	--	--
5	98.5 ^b	8.94	204	211	0.628	95	326	7.90	11.10
6	99 ^b	23.35	206	213	0.763	80	364	5.02	6.74
7	98.5	71.50	211	216	0.941	70	432	--	--

^a15 percent solids reaction mixture at 25°C

^bSecond reaction conducted for these samples



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Figure 15. Inherent viscosity versus TMA flow property relationship

Figure 17. The BTDA/BAC/2,4-DAT polymers flow less than the BTDA/HDA/2,4-DAT polymers at both temperatures as expected.

Interpretation of either flow test relevant to obtaining quality composites was needed at this juncture. Thus, if a 5 or 10 cm² press flow area was required to process prepregs at 100 psi then an inherent viscosity and temperature could be specified. Similar reasoning applies to the TMA flow test. The two flows are related. This is seen in Figures 12 through 14 where between a 5 to 10 cm² press flow area was obtained on the polymers at approximately the 50 percent TMA flow temperature.

Acurex-developed unidirectional polysulfone, carbon fiber prepregs from the early 1970s provide the following consolidation specifications.

- 260°C, 0.69 MPa, 5 min for flat composites
- 287°C, 1.04 MPa, 5 min for deep draw, 0.25-cm-thick cross-ply stock

The indicated processing temperatures are seen from Figure 10 to be equivalent to about 9.0 and 12 cm² press flow areas at 1.45 MPa and can be used as the basis of selection for processing the candidate compositions. Results presented in Figure 17 show that a BTDA/BAC/2,4-DAT polymer with an IV of 0.5 dl/g would have a press flow area of 10 cm² at 377°C. Initial selection of a polymer with an IV of 0.55 dl/g for a good balance between toughness and processability was recommended to NASA. Although blends of the BTDA/BAC/2,4-DAT and BTDA/HDA/2,4-DAT polyimides would have better flow properties, the loss in Barcol hardness discussed in the next section did not seem to justify this selection.

3.2.4 Barcol Hardness Testing of Polymers

Barcol hardness of selected moldings were measured at room temperature, 93°C and 140°C. These values are tabulated in Table 16. The values for the

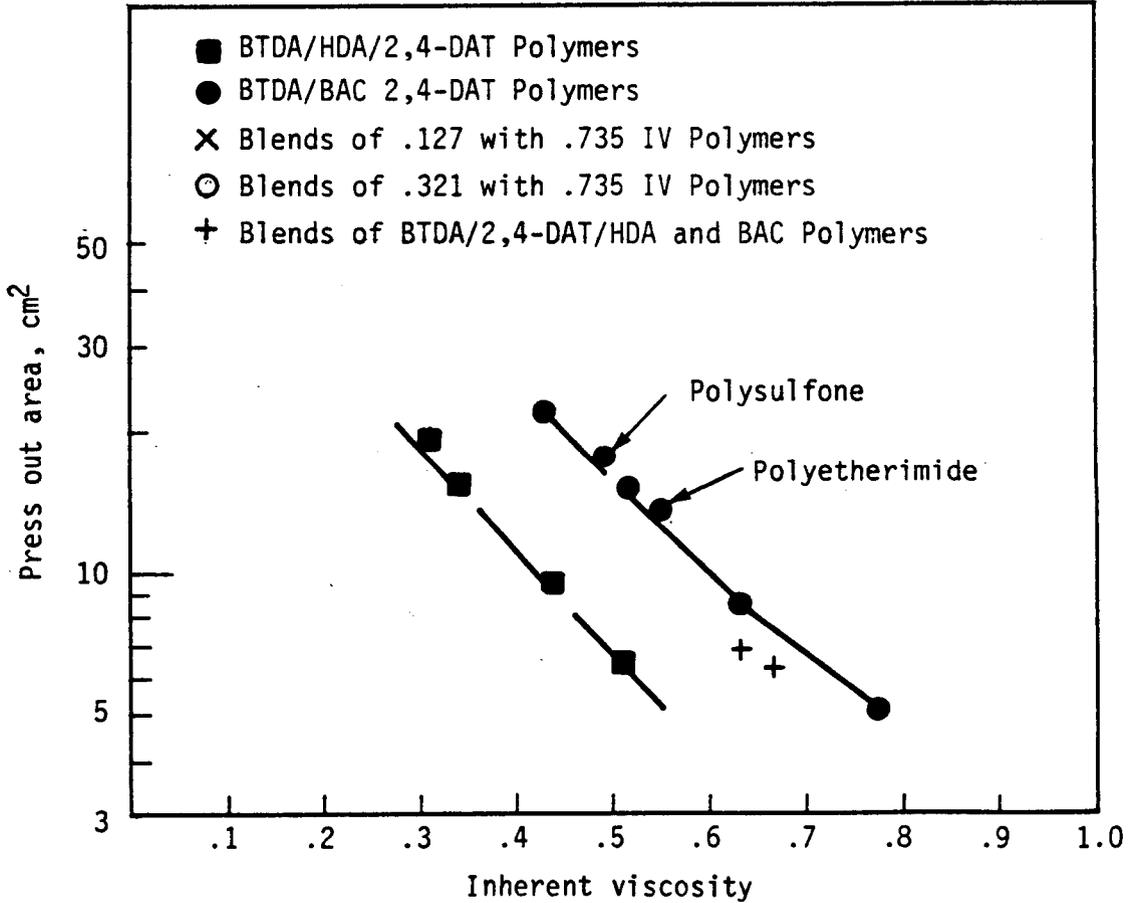
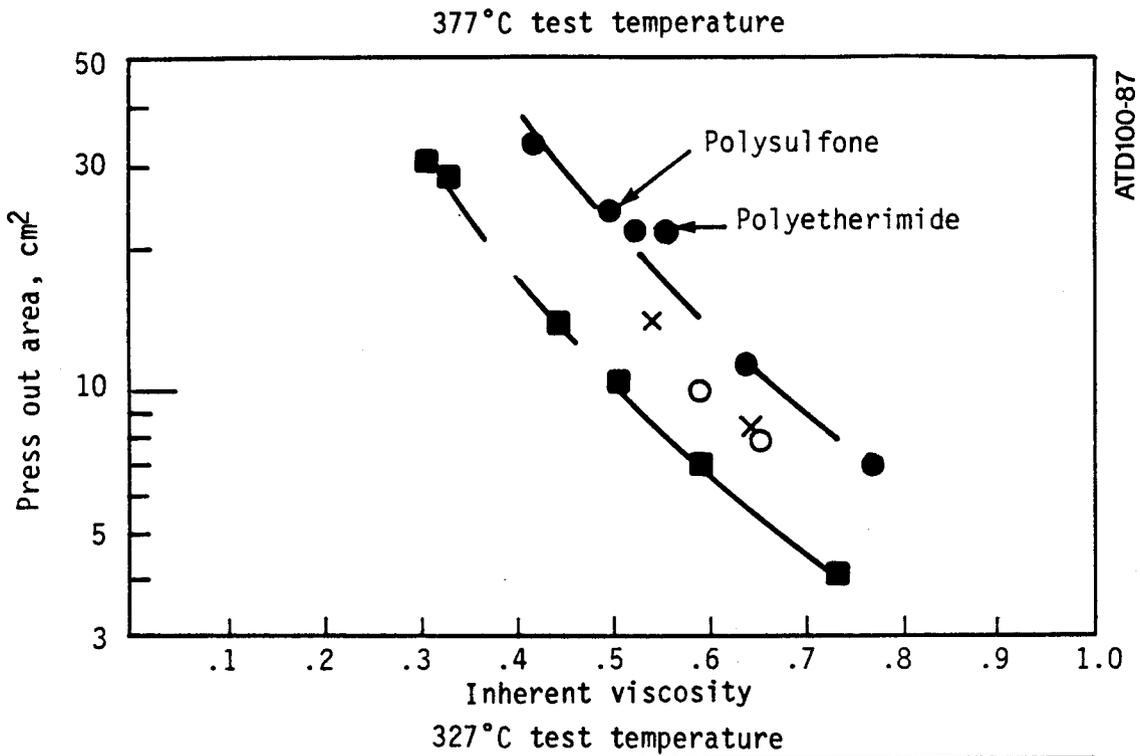


Figure 17. Inherent viscosity -- press flow relationship

Table 16. Glass transition temperature and Barcol hardness of molded polymers

Number	Polymer Composition	DSC Midpoint T _g (°C)	Barcol Hardness		
			RT Test	93°C Test	140°C Test
1	Polysulfone	187	34	30	30
2	Polyetherimide	217	36	27	22
3	BTDA/BAC/2,4-DAT Stoichiometry: 98.5% 99% 100%	243	50	42	42
		248	46	42	38
		232	50	45	42
4	BTDA/HDA/2,4-DAT Stoichiometry: 97.5% 98.5%	207	38	32	28
		211	38	32	28
5	Blends 40% BTDA/BAC/2,4-DAT ^a 60% BTDA/HDA/2,4-DAT ^b	226	46	40	33
6	40% BTDA/BAC/2,4-DAT ^c 60% BTDA/HDA/2,4-DAT ^b	230	47	40	33

^a0.336 IV polymer

^b0.736 IV polymer

^c0.436 IV polymer

polyimides with 2,4-DAT are very similar to the values previously obtained with m-PDA in Table 1. The blends of the BTDA/2,4-DAT/HDA and BAC polymers show values intermediate between the two parent polymers and are close to the values obtained on the BTDA/BDA/m-PDA polymer in Table 1.

3.3 COMPOSITE PROPERTIES AND SELECTION OF THE FINAL POLYIMIDE COMPOSITION

Carbon fabric composites were fabricated from the BTDA/HDA/2,4-DAT, BTDA/BAC/2,4-DAT, and the BTDA/HDA/BAC/2,4-DAT polyimides. Flexural strengths and moduli and shear strengths of the composites are listed in Table 17.

Final prepreg drying conditions, composite molding conditions, and the T_gs of the molded resins are provided in Table 18. The carbon fabric used in the composites was Celion 3000 (24 x 23), eight harness satin weave. The epoxy compatible size was removed with methylene chloride prior to impregnation. Impregnation occurred by the all-at-once addition of the 20-percent-solids varnishes to the carbon fabric on Teflon-coated glass to give a final resin volume (without cresol) of 40 percent. Cresol removal occurred by 20-hr treatment at 100°C in an air circulating oven. After 4 hr in the oven, the prepreg was turned over. This treatment was followed by 0.5-hr treatment at 180°C. Final prepreg drying correlations used for the composites are listed in Table 18.

With complete cresol removal, the calculated thickness for 60-volume-percent fiber, zero-void, and 7-ply composites is 0.25 cm (0.10 in). Since the resin solutions had been added to the fabric to provide this fiber volume, all of the composites were molded in air to 0.25-cm stops at less than 6.9 MPa pressure and at the temperatures indicated in Table 18.

The mechanical strengths of the composites from BTDA/2,4-DAT and HDA or HDA and BAC are excellent at both room temperature and 93°C. The 698⁺ MPa

Table 17. Carbon fabric composite properties of polyimide compositions

Composition	Laminate Number	Flexural Properties ^a Strength, MPa(ksi)/Modulus, GPa(msi)		Short Beam ^b Shear Strength, MPa(ksi)	
		Test Temperature (°C)		Test Temperature (°C)	
		Ambient	93°C	Ambient	93°C
BTDA/HDA/2,4-DAT	98-113	724(105)/53(7.7)	807(117)/59(8.6)	60(8.6)	56(8.0)
BTDA/HDA/2,4-DAT	98-103	--	--	51(7.3)	49(7.1)
BTDA/BAC/2,4-DAT	98-86	462(67)/59(8.5)	400(58)/58(8.4)	27(3.9)	25(3.5)
BTDA/HDA/BAC/2,4-DAT	98-112	765(111)/54(7.8)	861(125)/59(8.6)	59(8.4)	50(7.2)
BTDA/HDA/BAC/2,4-DAT	98-114	765(111)/56(8.1)	800(116)/59(8.5)	65(9.2)	57(8.2)

^aASTM D790-84a, 2 specimens per test

^bASTM D2344-84, 3 specimens per test

Table 18. Composite processing parameters and resin Tg

Composition	Laminate Number	Varnish Viscosity (Pa·s)	Final Prepreg Drying Conditions	Composite Molding Conditions	Tg of Molded Resin ^a (°C)	TGA Volatile Loss ^b (%)	Tg of Resin After TGA ^a (°C)
BTDA/HDA/2,4-DAT	98-113	30.5	30 min @ 260°C	2 min @ 349°C	206	0.5	211
BTDA/HDA/2,4-DAT	98-103	220.0	30 min @ 260°C	3 min @ 345°C	206	0.5	211
BTDA/BAC/2,4-DAT	98-86	32.6	30 min @ 260°C plus 20 min @ 343°C	2 min @ 377°C	243	0.3	246
BTDA/HDA/BAC/2,4-DAT	98-112	33.8	30 min @ 260°C	3 min @ 327°C	209	1.6	230
BTDA/HDA/BAC/2,4-DAT	98-114	33.8	30 min @ 316°C	2 min @ 349°C	230	0.3	233

^aDSC (inflection)

^bUnder high vacuum to 300°C

(100+ ksi) flexural strengths at 93°C are a significant improvement over the 551 MPa (80 ksi) flexural strength previously obtained at 82°C on the BTDA/HDA/m-PDA composite.² This strength improvement is clearly due to a change in failure modes. The 698+ MPa failures occurred on the compression side of the specimen with fracture of individual fiber tows. The 551 MPa failure also occurred on the compression side of the test specimen, however, fiber tows were pushed away from the specimen surface and were not fractured.

This change in failure modes is probably due to differences in the mechanical properties of the polymers. Although the substitution of m-PDA with 2,4-DAT may play a role (restricted rotation around the C-N bond due to the presence of the o-methyl group), the elevated temperature compression yield strengths were higher for the BTDA/HDA/m-PDA polymer when prepared from the Chriskev BTDA than the Gulf BTDA. This difference in compression yield strength is discussed in Section 3.1.4.

The increase flexural properties observed from room to elevated temperature testing is contrary to expectation. This increase is no doubt related to thermal stress relief at 93°C of residual cooldown stresses in the as-prepared composites. The 10- to 15-percent decrease in shear strengths with elevated temperature testing is not serious and shows an improvement over the 22 and 42 percent strength reduction obtained in the BTDA/HDA/m-PDA resin system.²

Photomicrographs of all of the composites showed that excellent flow had occurred during molding. All of the composites showed zero void contents, however, the composite with the BTDA/BAC/2,4-DAT matrix showed numerous microcracks in the matrix due to the mismatched coefficients of contraction of the fiber and the resin. The microcracked matrix is responsible for the low composite strengths seen for this resin system in Table 17.

Although the BTDA/BAC/2,4-DAT resin system had been recommended to NASA prior to composite testing for scale-up, in view of its poor composite properties it was subsequently recommended that the BTDA/HDA/BAC/2,4-DAT polyimide be scaled up. It is not clear why the BTDA/BAC/2,4-DAT polyimide microcracked when tested as a composite matrix, however, its higher prepreg drying temperatures and composite molding temperatures appear to be implicated. It was also learned during the above composite efforts that resin brittleness is increased by prepreg staging in air versus nitrogen at temperatures as low as 288°C (550°F). Thus, minimum drying cycles at elevated temperatures appear to be indicated until further efforts elucidate the cause(s) of matrix microcracking. Antioxidants may be needed.

3.4 SCALE-UP AND PROPERTIES OF THE SELECTED POLYMER

Synthesis of 4 kg of the selected polymer, BTDA/HDA/BAC/2,4-DAT was required for neat resin property determination and transmittal of 3.6 kg as a 20 percent solids solution to NASA. The selected polymer had a Brookfield viscosity of 33.8 Pa·s at 25°C in cresol at 20 percent solids. (See Table 18.)

The nominal molar fractions of the monomers in the BTDA/HDA/BAC/2,4-DAT polymer are: BTDA at 0.5, HDA at 0.125, BAC at 0.125, and 2,4-DAT at 0.25. End capping is accomplished with PA and the final stoichiometry contains 0.5 percent excess anhydrides. For example, synthesis of the BTDA/HDA/BAC/2,4-DAT polymer based on 1.00 mole of total amines at 99 percent stoichiometry used 0.99 mole BTDA (99 percent), 0.03 mole PA (1.5 percent) and 1.00 mole amines (100 percent).

Scale-up was readily accomplished by a 20-fold multiplication of the 0.3-mole synthesis which provided the composite properties given in Table 17. The procedure is outlined below and further details are given in Section 5.

The BAC was distilled and the remainder of the ingredients were used in the as-received condition. The BTDA was dried overnight under high vacuum at 175°C just prior to use. A portion of the cresol was added to a preweighed 22 l flask followed by addition of both aliphatic diamines. The powdered BTDA was added at room temperature to the stirring cresol solution of the amines. After 30 min reaction, the aromatic amine and the remainder of the cresol were added. The reaction was heated to 183°C with stirring and it was continued for 24 hr. Upon cooling to approximately 100°C, the solution was made up to 20 percent solids by the addition of fresh cresol. Samples were removed for Brookfield viscosity determination. The 99.0 percent stoichiometric reaction was determined to have a viscosity of 71.5 Pa·s at 25°C.

A second reaction at 97.8 percent stoichiometry produced a polymer solution with a viscosity of 15.4 Pa·s at 25°C.

Semilog extrapolation of the two solution viscosities showed that a 50/50-weight-percent blend of the two polymer solutions would produce a solution with a viscosity of 33.0 Pa·s at 25°C. Blending followed by stirring and warming to approximately 90°C produced three 12 l containers which had solution viscosities of 35.1, 34.1, and 34.8 Pa·s. The majority of the polymer solution (4.95 kg of polymer) was shipped to NASA on August 25, 1987.

The balance of the solution blend was diluted to 10 percent solids with chloroform and isolated with methanol to produce 577g of polymer. This polymer was molded at 343°C to produce the several moldings required for property determinations. The moldings were annealed for 24 hr at 200°C (30°C below the Tg of the polymer).

Properties of the neat molded BTDA/HDA/BAC/2,4-DAT polymer are listed in Tables 19 and 20. The properties seen in Table 19 for the selected polymer are between those for the BTDA/HDA/2,4-DAT and BTDA/BAC/2,4-DAT polymers. The 50 percent flow temperature by TMA flow test is 100°C above the Tg. This

agrees with the values in Figure 16 for this family of polymers. Barcol hardness is between those determined for the BTDA/HDA/2,4-DAT and BTDA/BAC/2,4-DAT polymers and listed in Table 16. The selected polymer, unlike those from m-PDA, is soluble in chloroform and methylene chloride and shows no resistance to paint strippers, but good resistance to hydraulic and deicing fluids.

Table 19. Properties of the BTDA/HDA/BAC/2,4-DAT polyimide

1. Inherent viscosity	0.55 dl/g
2. Tg	
DSC (onset)	228°C
DSC (inflection)	233°C
3. Barcol hardness	
RT	43
93°C	36
140°C	32
RT (after above tests)	47
4. Specific gravity	1.333 g/cc
5. TMA flow test	
50% flow temperature at 0.20 MPa (28 psi)	331°C
6. Solvent resistance	
Paint strippers	
-- Acid	80% dissolved in 16 hr
-- Nonacid	60% dissolved in 16 hr
Deicing fluid (stressed) ^a	Pass
Skydrol 500B (stressed) ^a	Pass
7. Wet properties (24-hr water boil)	
Dry FTUCL	231°C intercept 220°C deviation from linearity
Wet FTUCL	220°C intercept 161°C deviation from linearity
Weight gain	2.5%
8. Expansion coefficient	
20°C	43 $\mu\text{m}/\text{m}/^\circ\text{C}$
50°C	43 $\mu\text{m}/\text{m}/^\circ\text{C}$
90°C	47 $\mu\text{m}/\text{m}/^\circ\text{C}$
110°C	51 $\mu\text{m}/\text{m}/^\circ\text{C}$
170°C	56 $\mu\text{m}/\text{m}/^\circ\text{C}$
240°C (melt)	234 $\mu\text{m}/\text{m}/^\circ\text{C}$
Tg	225°C

^a5000 psi, 14 days

Table 20. Mechanical properties of BTDA/HDA/BAC/2,4-DAT polymer^a

Compression Properties (ASTM D 695)							
Stress at Proportional Limit, MPa (psi)		Stress at Yield, MPa (psi)		Modulus, GPa (psi x 10 ⁵)		Strain at Yield (%)	
RT	93°C	RT	93°C	RT	93°C	RT	93°C
98.6 (14300)	75.2 (10900)	214 (31000)	157 (22700)	3.82 (5.54)	3.16 (4.58)	9.50	8.57
Tension Properties (ASTM D 638)							
Stress at Proportional Limit, MPa (psi)		Stress at Failure MPa (psi)		Modulus, GPa (psi)		Strain at Failure (%)	
RT	93°C	RT	93°C	RT	93°C	RT	93°C
33.0 (4790)	28.3 (4100)	128 (18600)	93.7 (13600)	3.14 (4.56)	2.72 (3.95)	6.68	5.00

^aThree specimens per determination.

SECTION 4
CONCLUSIONS AND RECOMMENDATIONS

4.1 RESIN SYNTHESIS

- There are differences in the BTDA from two sources pertaining to reaction conditions in cresol required to achieve high-molecular-weight polymers.
- Cresol condensation of one source of BTDA with diamines provides a direct relationship between monomer concentration and IV attained (second order reaction). High IVs were attained, however, at low-monomer concentrations (5 percent) on prior phases of this program from another source of BTDA.
- Since the synthesis was readily scaled up to 15 kg of solution (3 kg polymer), it is concluded that relatively large batches of the polymer can be prepared without difficulty
- Extensive purification of the raw materials is not required. The BTDA was dried just prior to use and the BAC was distilled. The remainder of the ingredients were used in the as-received condition. All are commercially available.

4.2 RESIN PROPERTIES

- Reducing the linear aliphatic content of the program polyimide compositions increases the Tg as well as the Barcol hardness.

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Compression modulus and the stress at the proportional limit are also increased with reduced linear aliphatic contents.

- The stressed solvent resistance of the BTDA/m-PDA/BDA, HDA, and BAC polymers is excellent in deicing fluid and hydraulic fluids. In two paint stripper compositions used on commercial aircraft, their stressed solvent resistance is unacceptable even though their resistance to chloroform is excellent. The action of the phenol or other organic acid present in paint strippers in combination with the halogenated solvent attacks polyimides as well as all other thermosets and thermoplastics tested. Reformulation of paint strippers is required before their use on composites will be acceptable.
- The stressed solvent resistance of the BTDA/HDA/BAC/2,4-DAT polymer is excellent in deicing and hydraulic fluids. This polymer composition is soluble in chloroform, methylene chloride, and two paint strippers. Chloroform solubility is no doubt due to use of the 2,4-DAT in place of the m-PDA in the composition.
- BTDA/m-PDA/BDA, HDA, and BAC polymers showed good fracture toughness and moisture resistance relevant to the intended application in composites.

4.3 MOLECULAR WEIGHT/MELT FLOW PROPERTIES

- High-molecular-weight BTDA/m-PDA/BDA, HDA, and BAC polyimides and BTDA/2,4-DAT/HDA and BAC polyimides readily provide thick moldings at 6.9 MPa and temperatures less than 100°C above their respective T_gs.
- Thin moldings (0.20 g/cm²) are not successfully prepared by the conditions cited above from high-molecular-weight BTDA/m-PDA/BDA, HDA, and BAC polyimides or the BTDA/2,4-DAT/HDA and BAC polyimides.

- Low-pressure thin moldings are prepared from the cited polymers with reduced molecular weights (IVs of less than ~ 0.6 dl/g).
- Molecular-weight reduction by either stoichiometric imbalance or end capping does not provide the expected improvement in melt flow properties when the aromatic amine is m-PDA. This is due to crystallization of intermediates upon evaporation of the solvent from the polymer. Isolation of the polymers from clear cresol solutions with methanol gives polymers which give the expected melt flow properties after molding at 303°C for 30 min.
- When the aromatic diamine used in the polyimides is 2,4-DAT or 2,6-DAT, intermediate crystallization does not occur and the expected improvements in melt flow properties are obtained upon solvent evaporation.
- Melt viscosities of neat polymers which have the same solution viscosities will be very close if not the same. Reproducible solution viscosities are achieved by the blending of two polymer solutions which, by end capping, have viscosities above and below a target viscosity value. This is probably only achievable with completely imidized polymers. The prognosis to achieve this high degree of melt viscosity reproducibility from PMR approaches is poor. This latter approach was studied in detail in Phase III efforts of this program.

4.4 PREPREGS

- Carbon fabric prepregs were readily prepared from 20 percent solids varnishes with good fiber bundle impregnation
- Smoothed prepregs were not required to prepare zero void composites due to the good melt flow properties of the resins

4.5 COMPOSITE PROPERTIES

- The 7-ply Celion carbon fabric composites prepared from the BTDA/HDA/2,4-DAT and BTDA/HDA/BAC/2,4-DAT polyimides had excellent flexural and good shear properties at room temperature and 93°C. (The epoxy size on the carbon fabric had been removed with methylene chloride).
- The 7-ply Celion carbon fabric composite prepared from the BTDA/BAC/2,4-DAT had poor flexural and shear properties due to microcracking of the resin matrix. This may be due to the higher prepreg drying and molding temperatures used in its preparation than the two polyimides mentioned above. Processing the prepreg and composite in air may also have played a role in the microcracking.
- The composites prepared on this Phase IV effort were readily prepared void free with rapid heating and cooling cycles at pressures of less than 6.9 MPa. This is in distinct contrast to Phase III composite efforts with polymers in which no control was exercised over the molecular weight of the polymers.

4.6 PROGRAM OBJECTIVES

With the limited testing conducted on the BTDA/2,4-DAT/aliphatic amine polyimides to date, it is concluded that this class of polymers holds excellent potential to meet all of the program objectives detailed in Section 2, with the exception of stressed resistance to chlorinated solvents and paint strippers. The initial composite properties, in particular, are most attractive.

SECTION 5
EXPERIMENTAL

Procedure for Study of Reaction and Stoichiometry Conditions to Produce Polyimides in Cresol

Silicone oil in a large crystallizing dish was heated to 180°C on a hotplate equipped with magnetic stirring capability. Fifteen grams (0.04655 mole) of BTDA was weighed into a 250 ml erlenmeyer flask on an analytical balance. A preweighed Teflon-coated magnetic stirring bar and 150 ml of cresol were added to the flask which was placed in the hot oil bath to dissolve the BTDA. The flask was cooled in an ice bath to room temperature and 2.705g (0.02328 mole) HDA was quantitatively washed into the flask with small portions of cresol. The reaction was allowed to stir for 45 min at room temperature. This was followed by a 1 hr and 15 min treatment under nitrogen in the 180°C oil bath. After cooling to room temperature, 2.416g (0.02328 mole) m-PDA dissolved in 5g cresol was quantitatively transferred into the flask. The reaction was stirred under nitrogen for 1 hr and 20 min in the hot oil bath, cooled to room temperature, and the weight of solution determined to be 159.2g. Based on calculated polymer weight, the solution contained 11.75 percent polymer.

A small sample was removed from the reaction and diluted to 0.5 percent by weight polymer in cresol. The relative viscosity of the sample was determined at 25°C. The solids content of the viscosity sample was determined by evaporating a weighed portion of the solution to dryness in an

air-circulating oven for 30 min each at 150° and 225°C. The cresol weight-loss from the sample was converted to milliliters for calculation of the inherent viscosity of the sample. It was 0.46 at 0.5 dl/g at 25°C.

Aliquots of the reaction were taken and reacted at 180°C with diamines and/or cresol added to give selected adjustments to the stoichiometry or solids content. Samples were removed from the completed polymerizations for inherent viscosity determination as described above. Figure 3 of this report indicates the reaction conditions and stoichiometries studied.

A second reaction was conducted along the lines described above, however, it was at a higher solids content and the m-PDA was not reacted prior to taking aliquots for further reactions. Thus, 29.3328g of BTDA (0.09103 mole) was dissolved in 90g of cresol with heat. The BTDA-cresol solution was cooled to 14°C and 5.3113g (0.04533 mole) of HDA in 5g of cresol was added with rapid stirring. Transfer from the weighing container was completed with small portions of cresol. The reaction was heated in a 180°C oil bath for 2 hr and 20 min. After cooling to room temperature, 4.4370g (0.04103 moles) of m-PDA dissolved in 8g of cresol was added. The weight of the solution was 127.4g which represents a solids content of 23.53 percent. The diamine/BTDA stoichiometry was calculated to be 95.26 percent. As discussed above, aliquots of this reaction mixture were diluted with cresol and/or the stoichiometry adjusted with m-PDA or MDA for further reaction. Figure 4 of this report shows the stoichiometries and solids contents of reaction conditions studied.

98.5 Percent Stoichiometric BTDA/HDA/2,4-DAT Polymer

A 2 l flask equipped with stirrer and nitrogen inlet was weighed and set up with heating mantle and stirring motor. To the flask, 29.0540g (0.2500 mole) HDA and 500 ml of cresol was added. BTDA dried at 175°C in a

vacuum oven overnight was weighed into a 400-ml beaker. The 158.7g (0.4925 mole) of BTDA and 2.9642g (0.0200 mole) PA were added to the stirring cresol solution of HDA at room temperature. Fresh cresol (250 ml) was used to transfer the anhydrides into the flask. To the stirring solution, 30.5425g (0.2500 mole) of 2,4-DAT was added. The flask and contents were placed on a balance and the total solution weight increased to 1009.8g. After 24-hr reaction under a nitrogen blanket at temperatures between 190° and 200°C, the flask was cooled, reweighed, and the solution weight brought up again to 1009.8g. The Brookfield viscosity of the 20 percent solids solution at 25°C was determined to be 30.5 Pa·s.

99.0 Percent Stoichiometric BTDA/HDA/BAC/2,4-DAT Polymer

To a preweighed 22 l flask equipped with stirrer, 248.94g (1.750 mole) BAC, 203.21g (1.750 mole) melted HDA and 7 l cresol were added. To this rapidly stirring solution was added 2233.05g (6.930 mole) BTDA and 31.105g (0.210 mole) PA from two 4 l beakers. The BTDA had been dried the previous night at 175°C under high vacuum. After 30 min of stirring, 427.60g (3.500 mole) of 2,4-DAT was added. The flask with contents was placed on a scale and the solution weight increased to 14,391g. After 24 hr of reaction with stirring under a nitrogen blanket at temperatures between 185° and 195°C, the flask was cooled, weighed, and the solution weight brought up to 14,391g a second time. The Brookfield solution viscosity at 25°C was determined to be 71.0 Pa·s.

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1. Delano, C. B., and C. J. Kiskiras, "Development of an Impact- and Solvent-Resistant Thermoplastic Composite Matrix," NASA CR 172285, April 1984.
2. Delano, C. B., and C. J. Kiskiras, "Development of an Impact- and Solvent-Resistant Thermoplastic Composite Matrix -- Phase III," NASA CR 172568, June 1985.
3. Delano, C. B., J. D. Dodson, and R. J. Milligan, "Extended Flow Life Laminating Designs," AFML-TR-77-158 (1977).
4. Delano, C. B., A. H. McLeod, and C. J. Kiskiras, "Synthesis of Improved Phenolic and Polyester Resins," NASA CR-165180, September 1980.

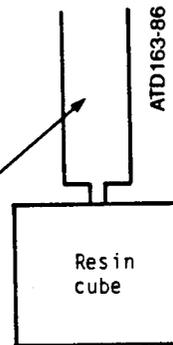
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APPENDIX A
FAILURE TEMPERATURE UNDER COMPRESSION LOAD

Acurex screens for upper use temperature by placing a cube of resin in the TMA and determining the temperature where the expansion curve deviates from linearity. With a 100g weight on the penetration probe, curves similar to those indicated in Figure A-1 are obtained. Some resins after water boil show a change in slope with water loss above 100°C. This slope change gives a deviation from linearity but is not interpreted as failure temperature since resin softening may not occur until a much higher temperature is reached. Acurex calls this test "failure temperature under compression load" (FTUCL). Inspection of the curves in Figure A-1 shows that deviation from linearity can precede resin softening by several hundred degrees if the resin system has crystallinity. Extrapolation of the expansion curve with the softening curve provides an intercept temperature which is closer to the heat distortion temperature described in ASTM D648. The three curves shown in Figure A-2 show the behavior of the crystalline polyimides from PMDA with C₆, C₈, and C₁₂ diamines. These three polymers exhibit thermal crystallization. Figure A-3 shows the behavior of the amorphous polyimides from BTDA with the same three diamines. Penetration occurs before the glass transition temperature is reached. Increasing diamine aliphatic chain length in both series of polyimides reduces the upper use temperature. The high FTUCL of the polyimide from BTDA with isophoronediamine shows the expected result from the use of the cycloaliphatic compared to linear diamines.

Failure temperature under compression load (FTUCL)

100g weight on TMA penetration probe



450 psi

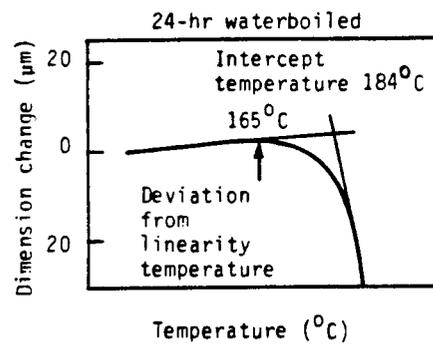
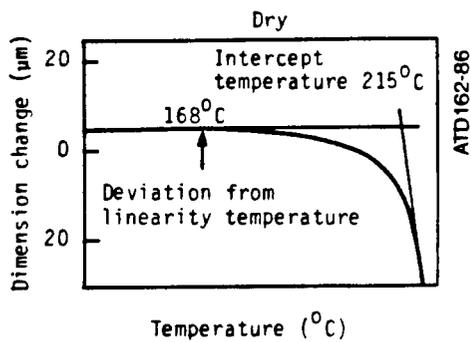


Figure A-1. Procedure for determining upper use temperature

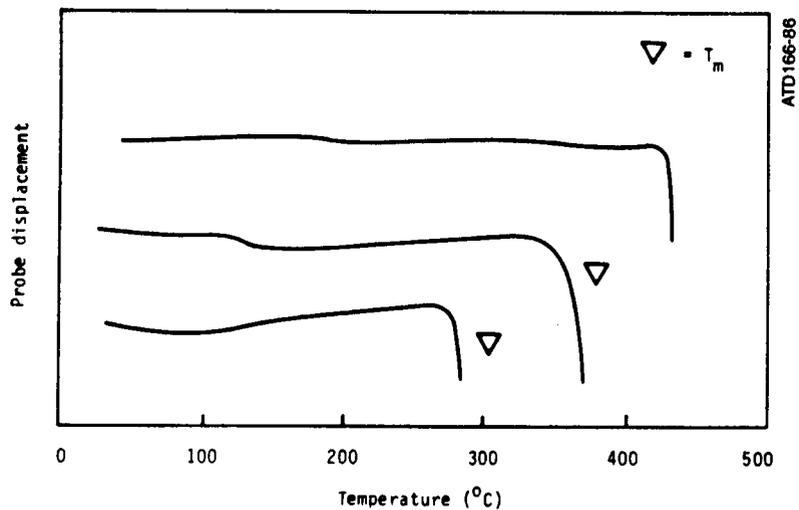


Figure A-2. FTUCL curves for PMDA with C6, C8, and C12 diamines

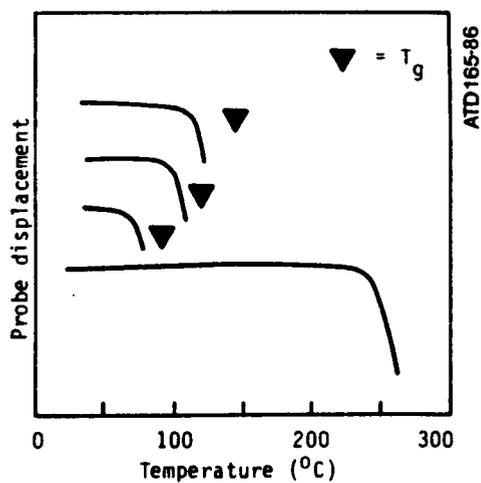


Figure A-3. FTUCL curves for BTDA with C6, C8, C12, and isophorone diamines

APPENDIX B

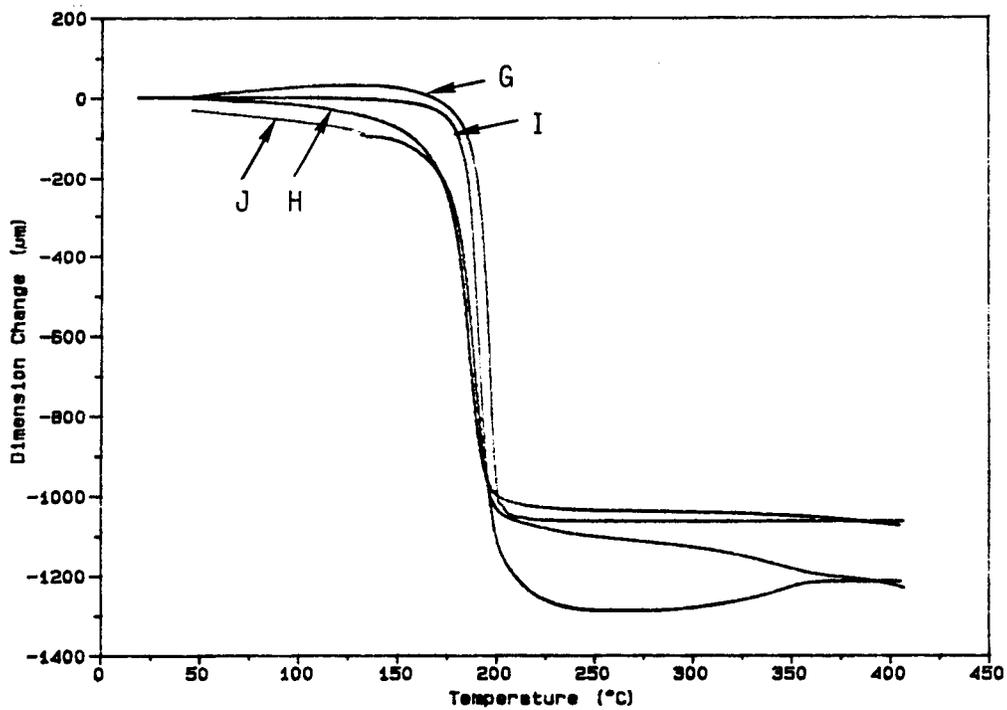
TMA FLOW TEST METHOD DEVELOPMENT

B.1 FIBEROUS POLYMERS

Prior testing on fibrous polymers utilized a 100g weight on the DuPont TMA expansion probe in combination with DSC cups to contain the polymer.¹ The large downward displacement of the probe demonstrated flow or a volume collapse of the fibrous polymer near the Tg. Use of this procedure on the BTDA/HDA/m-PDA polymer fibers with varying inherent viscosities provided the result seen in Figure B-1. Clearly the probe displacement is associated with the Tg of the polymers; however, no information on melt properties of the polymers is obtained since the fibers are not molten at 200°C, the temperature at the end of the downward probe displacement.

B.2 MOLDED POLYMERS

As discussed below, the test described above gives a good indication of the melt flow characteristics of molded polymer specimens. Flow curves were obtained on several molded polymer samples at two pressures. Approximately 0.086 MPa (12.5 psi) pressure was obtained by placing a 100g weight on the TMA expansion probe in combination with the DSC cup on the sample to protect the probe. A 0.90 MPa (130 psi) pressure was obtained by placing a 457g weight on the probe with 0.0025-cm (1 mil) thick aluminum foil on the sample to protect the probe. The area for the 0.90 MPa pressure was calculated from the probe dimensions with no correction for the increased area caused by the thin aluminum foil. Use of small, thin-resin specimens, which were typically



Note: Inherent viscosities of samples
 Sample I = 0.30 dl/g
 Sample H = 0.37 dl/g
 Sample J = 0.62 dl/g
 Sample G = 1.59 dl/g

Figure B-1. Low-pressure flow curves of BTDA/HDA/m-PDA fibrous polymers

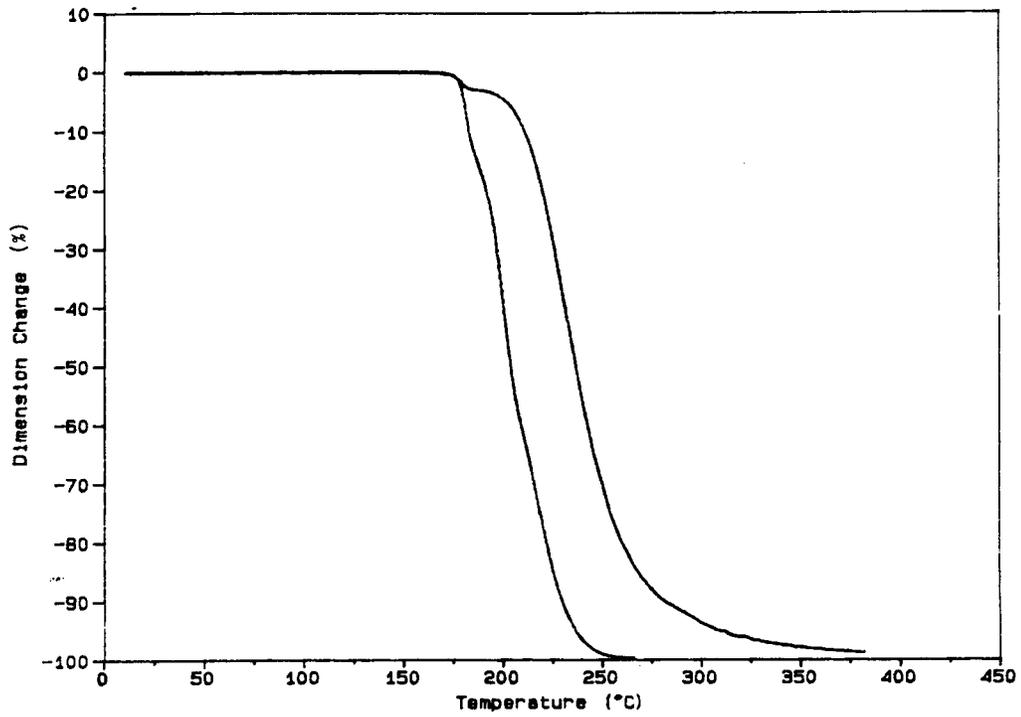
0.3 mm to 0.7 mm thick, placed on stainless steel foil prevented the melting polymer from contaminating the bottom of the holder and the thermocouple.

Flow curves for a number of polymer compositions are provided in Figures B-2 through B-5. Two curves are given in each figure. The top curve was obtained at the 0.086 MPa pressure and the bottom curve at the 0.90 MPa pressure. Flow curves for polysulfone (UDEL P1700) and polyetherimide (Ultem P1000) are provided in Figure B-2 for reference to two injection moldable polymers.

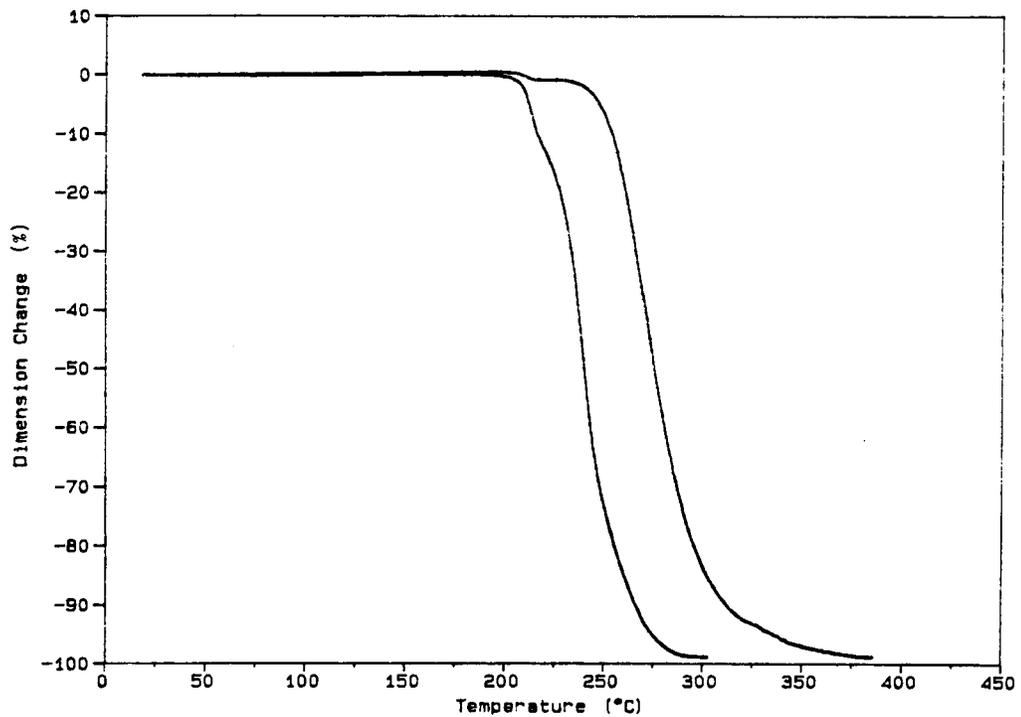
Figure B-3 provides flow for the polyimides from BTDA with 1,6-hexanediamine (HDA) or with 1,8-octanediamine (ODA). The BTDA/ODA polymer has a higher flow onset temperature than the BTDA/HDA polymer due to its crystallinity. This was a program first. Its T_m is 215°C with a ΔH of 17 joules/gram. It crystallized during slow cooldown from its molding temperature of 303°C.

Figures B-4 and B-5 provide flow curves for the first three program polymers: BTDA/BDA/m-PDA, BTDA/HDA/m-PDA, and BTDA/BAC/m-PDA. Flow curves for all of the polymers presented in Figures B-2 through B-5 show at least two features in common. A slight volume decrease is seen near the T_g (or T_m) of the polymer. The magnitude of this volume decrease is directly related to the applied pressure. Polymer melt temperatures (PMT) are probably very close to the onset temperature of the low-pressure flow curves. With high-molecular-weight aliphatic-aromatic polyimides, these temperatures are close to the polymer decomposition temperatures.

Both of the injection moldable resins (Udel P1700 and Ultem 1000) give flow curves at low pressure which are parallel to the higher pressure curves. This is in distinct contrast to the behavior of aliphatic-aromatic polyimides at the two pressures. Essentially no useful flow is observed at low pressure, but flow is induced by high pressure.



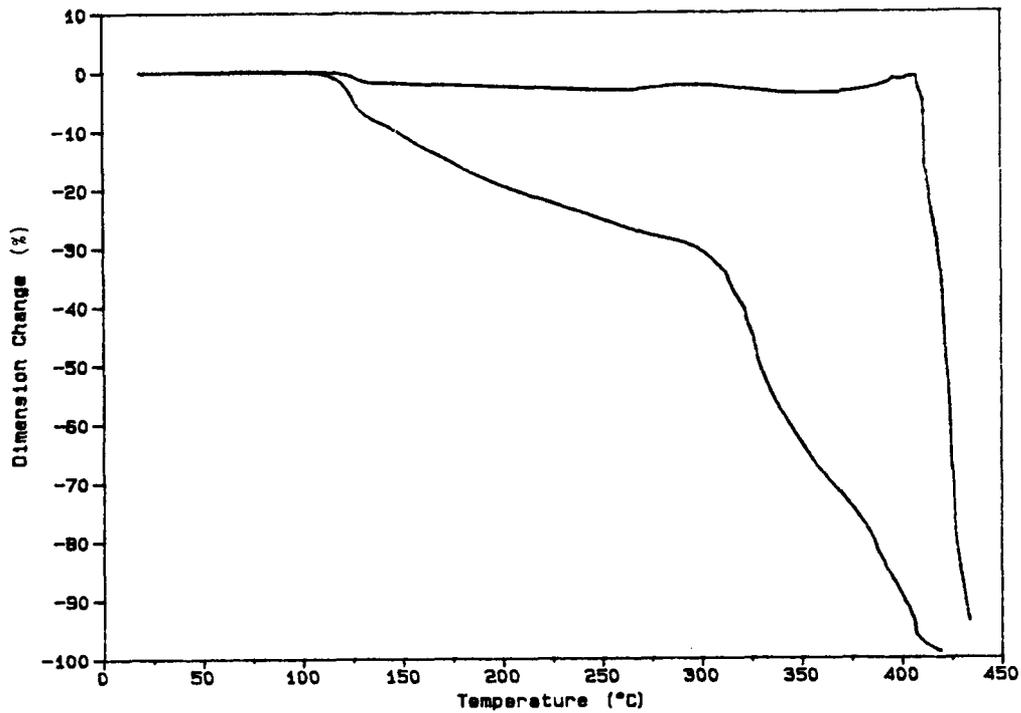
(a) Polysulfone



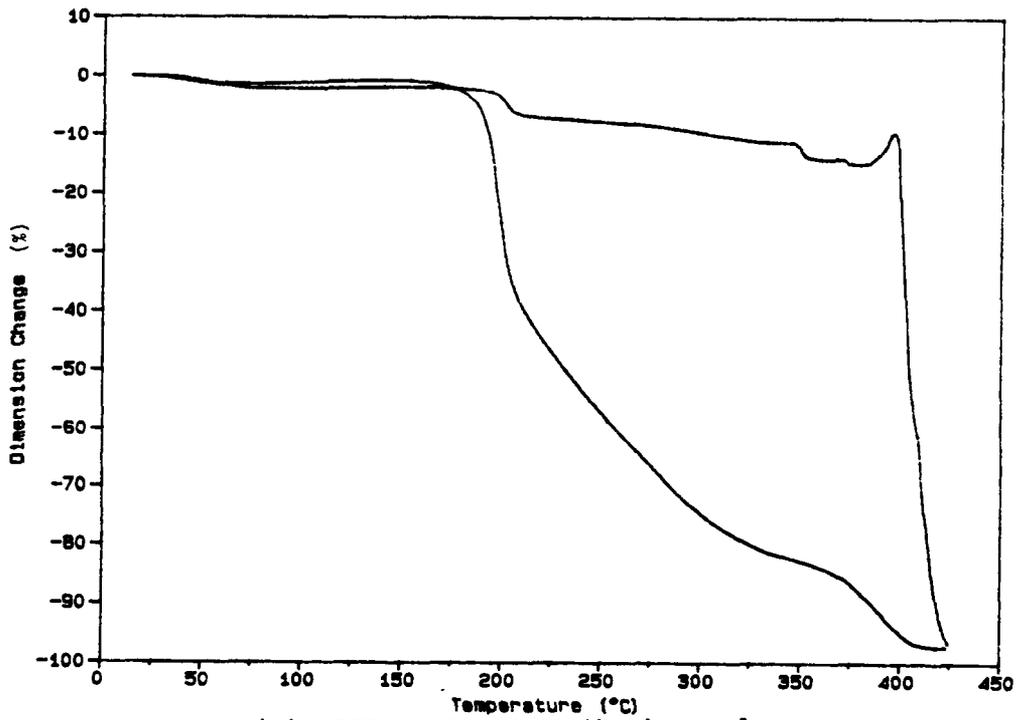
(b) Polyetherimide

Note: Top curves are at 0.086 MPa pressure,
bottom curves are at 0.90 MPa pressure.

Figure B-2. Flow curves of commercial thermoplastics



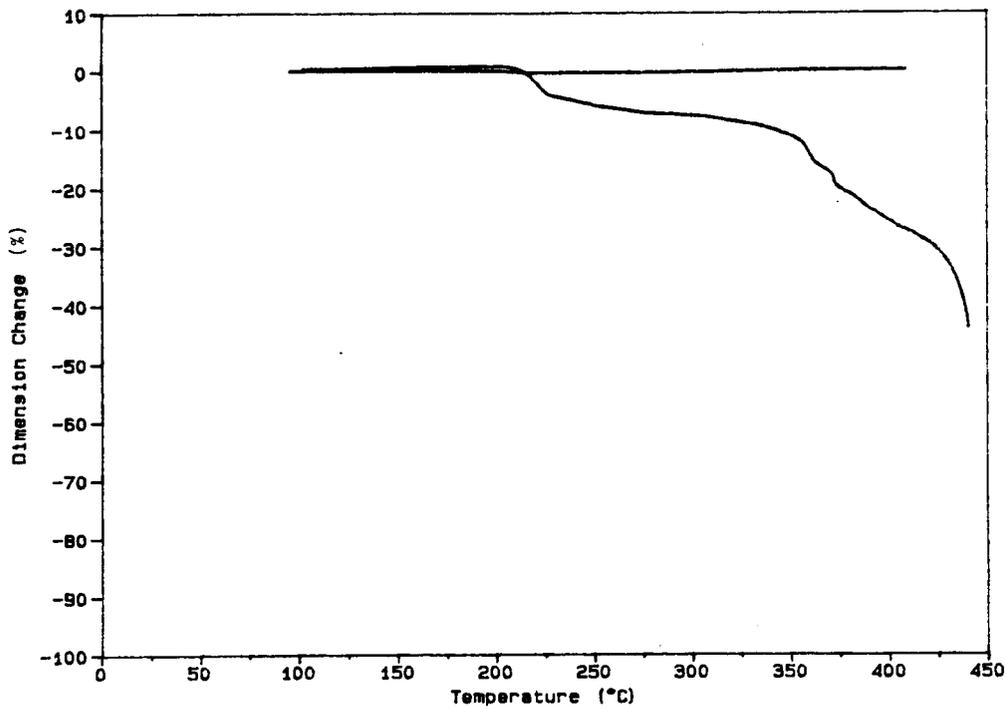
(a) BTDA/1,6-hexanediamine polymer



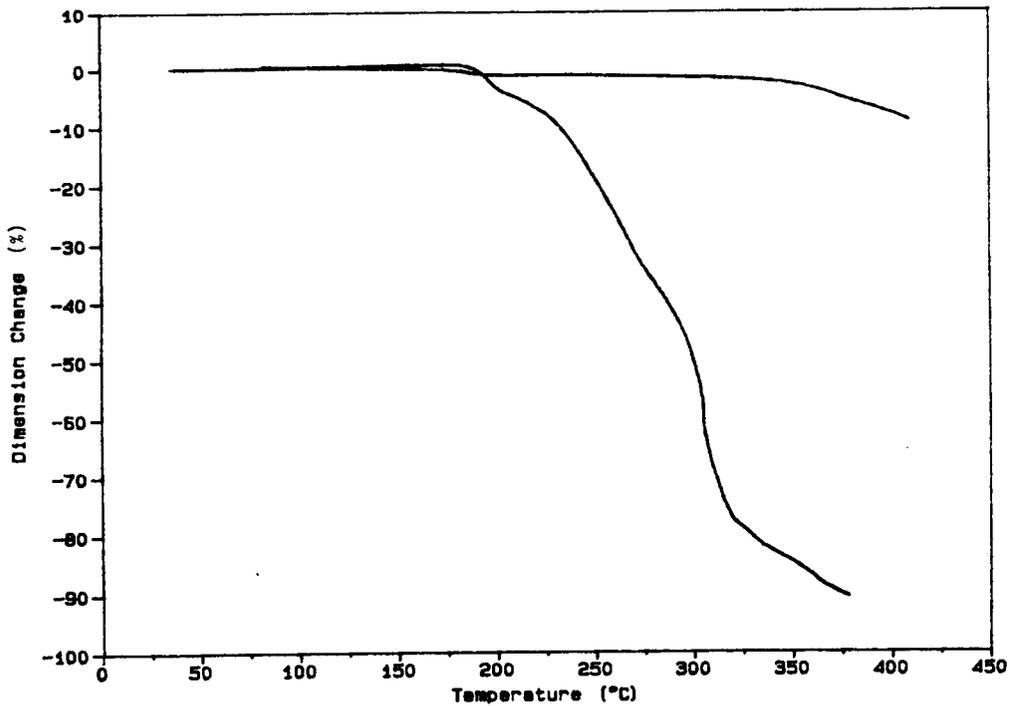
(b) BTDA/1,8-octanediamine polymer

Note: Top curves are at 0.086 MPa pressure,
bottom curves are at 0.90 MPa pressure.

Figure B-3. Flow curves of BTDA with two aliphatic diamines



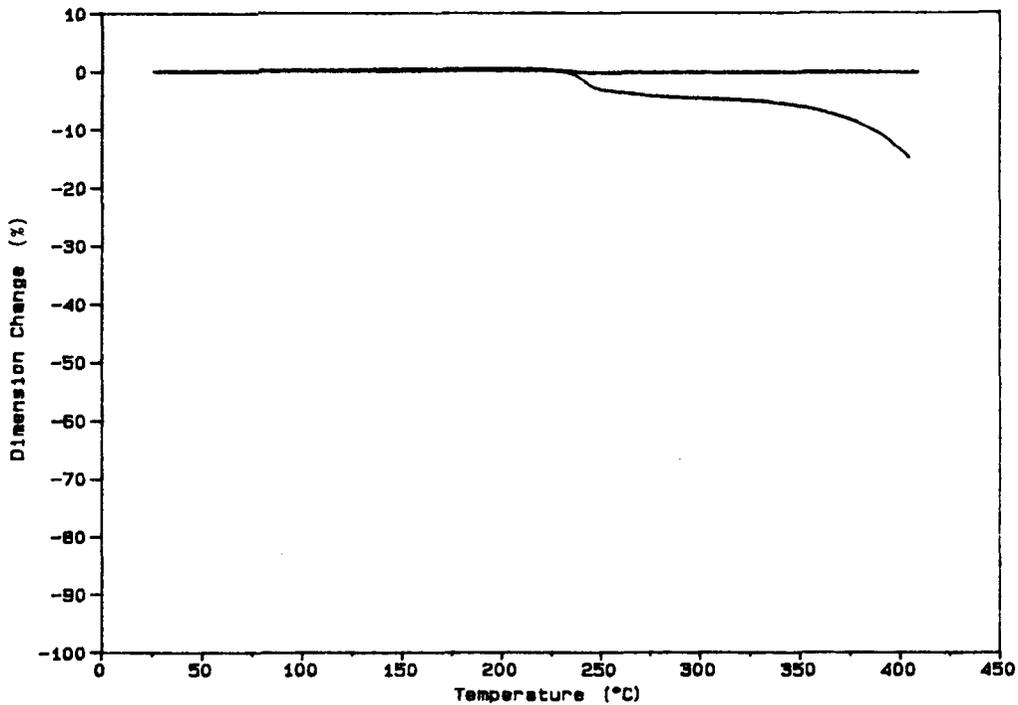
(a) BTDA/BDA/m-PDA polymers



(b) BTDA/HDA/m-PDA polymer

Note: Top curves are at 0.086 MPa pressure,
bottom curves are at 0.90 MPa pressure.

Figure B-4. Flow curves of BTDA/BDA/m-PDA and BTDA/HDA/m-PDA polymers



BTDA/BAC/m-PDA polymer

Note: Top curve is at 0.086 MPa pressure,
bottom curve is at 0.90 MPa pressure.

Figure B-5. Flow curves of BTDA/BAC/m-PDA polymer

contrast to the behavior of aliphatic-aromatic polyimides at the two pressures. Essentially no useful flow is observed at low pressure, but flow is induced by high pressure.

APPENDIX C

END CAPPING OF BTDA/BAC/m-PDA POLYMER WITH PHTHALIC ANHYDRIDE

The efforts described below were all with BTDA/BAC/m-PDA and phthalic anhydride (PA) at a BTDA stoichiometry of 97.5 percent. Opacity is developed in reactions containing less than 99.0 percent stoichiometry (BTDA = 1.000 mole, amines = 0.990 mole or BTDA = 0.990 mole, amines = 1.000 mole, PA = 0.020 mole) and the quantity of opacity developed is directly related to the stoichiometry. Reactions at 95 percent stoichiometry have more opacity than reactions with 96 percent stoichiometry, etc.

C.1 REACTION CONDITIONS AND OPACITY

These investigations addressed the issue of reaction conditions and opacity. Specifically, do reaction conditions exist which will lead to clear polymers at 97.5 percent BTDA stoichiometry? Opacity is developed in the reaction (if it develops) with increasing reaction times at 180°C after the m-PDA addition and by evaporation of the solvent from clear cresol solutions at 180°C. The latter phenomenon is no doubt the same effect noted last year² with 100 percent BTDA or amine stoichiometries and prepreg staging. At that time, prereaction of the aliphatic amine with the BTDA at 180°C prior to the m-PDA addition and addition of a small quantity of butanol were found to eliminate the opacity developed in the prepregs.

BTDA and PA were condensed with BAC for 2 hr at 180°C after addition of a cresol solution of the BAC in an ice-bath-cooled clear cresol solution of

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the anhydrides. A cresol solution of the *m*-PDA was added to the reaction and divided into portions. The solids content of each portion was adjusted to a nominal 15 percent with cresol, N-methylpyrrolidinone (NMP) and butanol. Each portion was condensed at 180°C and samples withdrawn with increasing reaction time. All of the reactions were heated for 16 hr at 180°C.

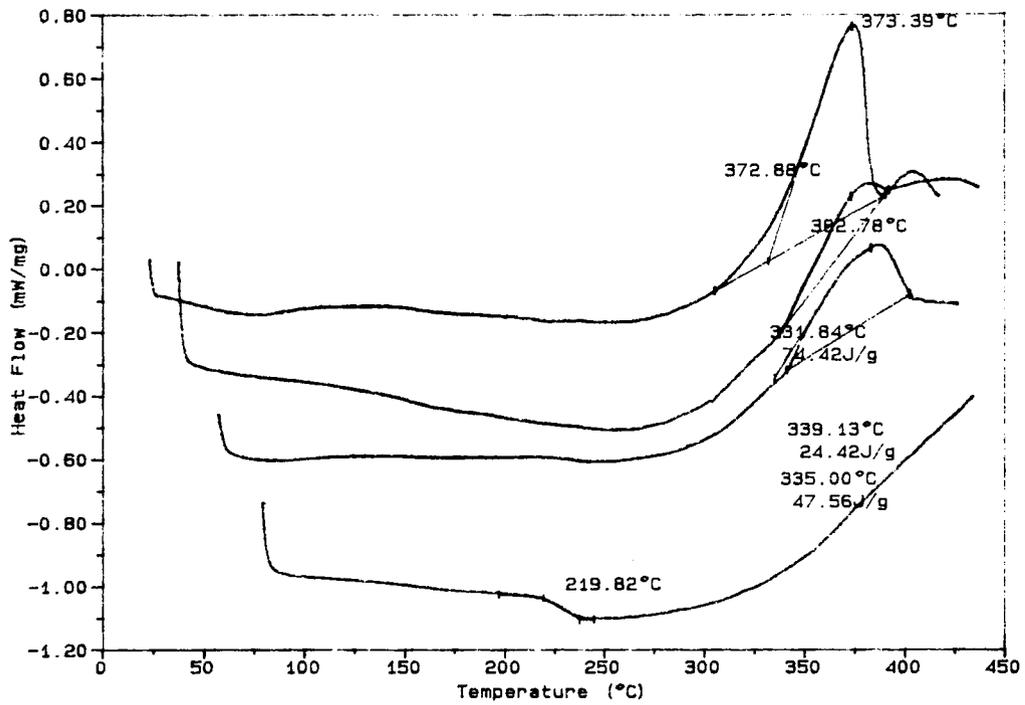
Opacity developed in the reaction to which NMP had been added within 30 min in the 180°C oil bath. Only a trace of opacity developed in the control containing only cresol. Slightly more than a trace of opacity developed in the reaction containing butanol. Removal of the cresol from the samples at 180°C in an air-circulating oven lead to increased opacity over that visible in the reaction in the NMP and control samples but very little in the butanol samples. Increasing reaction times reduced the opacity in all of the samples after cresol removal.

DSC analysis was conducted on numerous samples and Figures C-1 and C-2 show four curves for samples obtained from various treatments. The treatments are given below and are represented in each figure as the top to bottom curves, respectively.

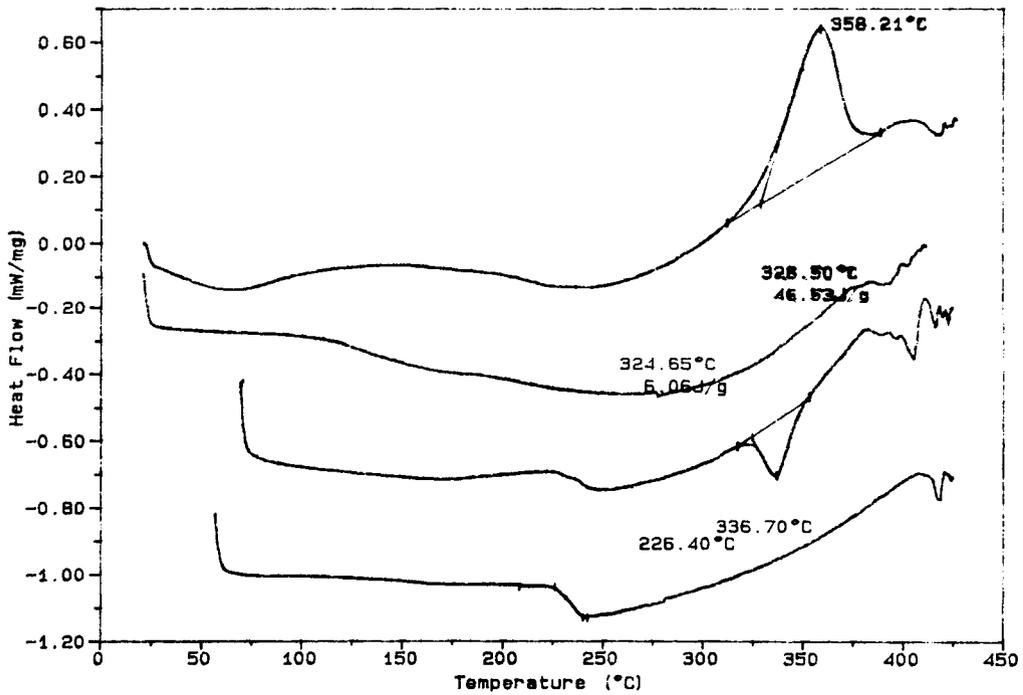
- Top curve: 2-hr reaction plus 2 hr in 180°C oven
- Second curve: 16-hr reaction plus 2 hr in 180°C oven
- Third curve: 16-hr reaction plus 2 hr in 180°C oven and 1 hr in 329°C oven
- Fourth curve: reheat of DSC specimen which gave third curve

Inspection of the DSC curves from the three reactions shows the following items:

- There is a high-temperature exotherm evident in the NMP diluted reaction in both of the 2- and 16-hr samples. This exotherm persists through a 1 hr at 329°C drying condition but is

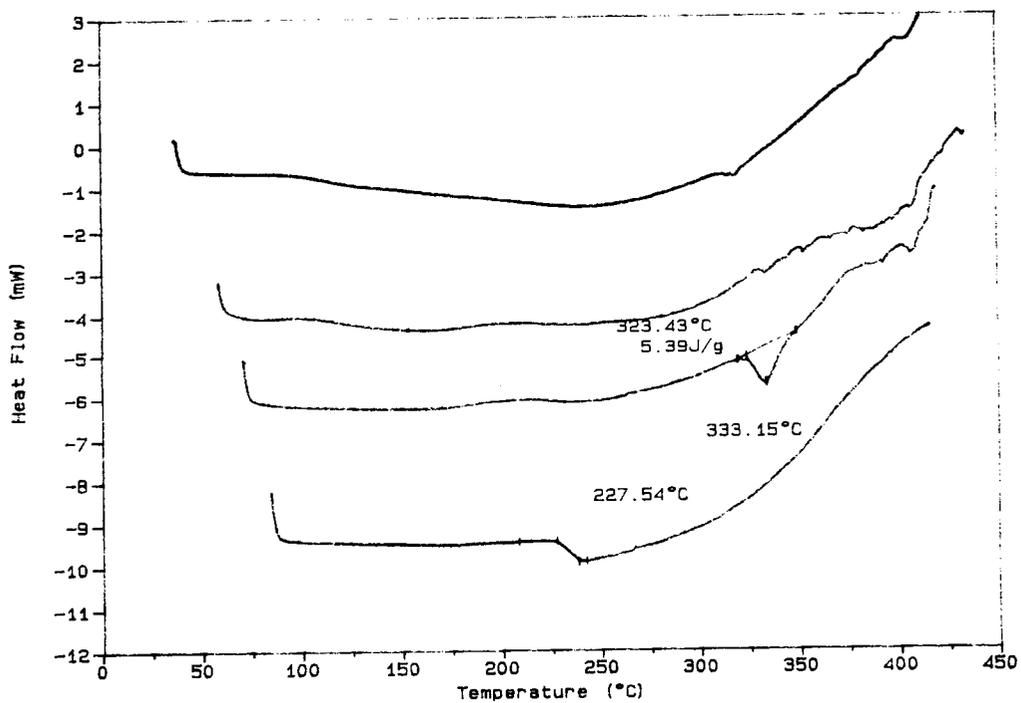


(a) Samples from NMP modified cresol reaction



(b) Samples from cresol reaction

Figure C-1. DSC curves of BTDA/BAC/m-PDA/PA polymers



Samples from butanol modified cresol reaction

Figure C-2. DSC curves of BTDA/BAC/m-PDA/PA polymers

eliminated with 425°C treatment. There is no evidence of an endotherm. This reaction had a lot of opacity.

- The 2-hr cresol sample showed an exotherm whereas the 16-hr sample did not. Visually, this is consistent with the quantity of opacity in the respective samples. Treatment of the 16-hr samples for 1 hr at 329°C gave an endotherm at 337°C.
- The butanol diluted samples showed no exotherm or increase in opacity upon cresol evaporation. The 329°C treated sample gave an endotherm at 333°C.
- Baseline instability at high temperature seen in the cresol and butanol reactions were attributed to continued loss of volatiles
- The cresol and butanol samples have final Tgs close to 227°C whereas the NMP sample achieved a Tg of only 220°C
- None of the samples exhibit a distinct Tg until they are heated to very high temperatures

Flow curves for the 329°C treated samples are provided in Figure C-3. A pressure of 0.90 MPa was used. The curve from the NMP reaction appears to initially show better flow characteristics, however, this is lost at higher temperatures. Both the cresol and butanol samples show a plateau above the Tg with a sharp knee in the melt curve at about 325°C.

C.2 POLYMERS FROM CRESOL

The absence of high-temperature exotherm in the butanol-cresol samples discussed above prompted investigation on the influence methanol isolation might have on the flow properties of such polymers. A 97.5 BTDA stoichiometry reaction with phthalic anhydride end capper was carried out for 16 hr at 180°C followed by 3 hr at 232°C (refluxing cresol). The solids content in the 75 percent cresol, 25 percent toluene mixture was 15 percent.

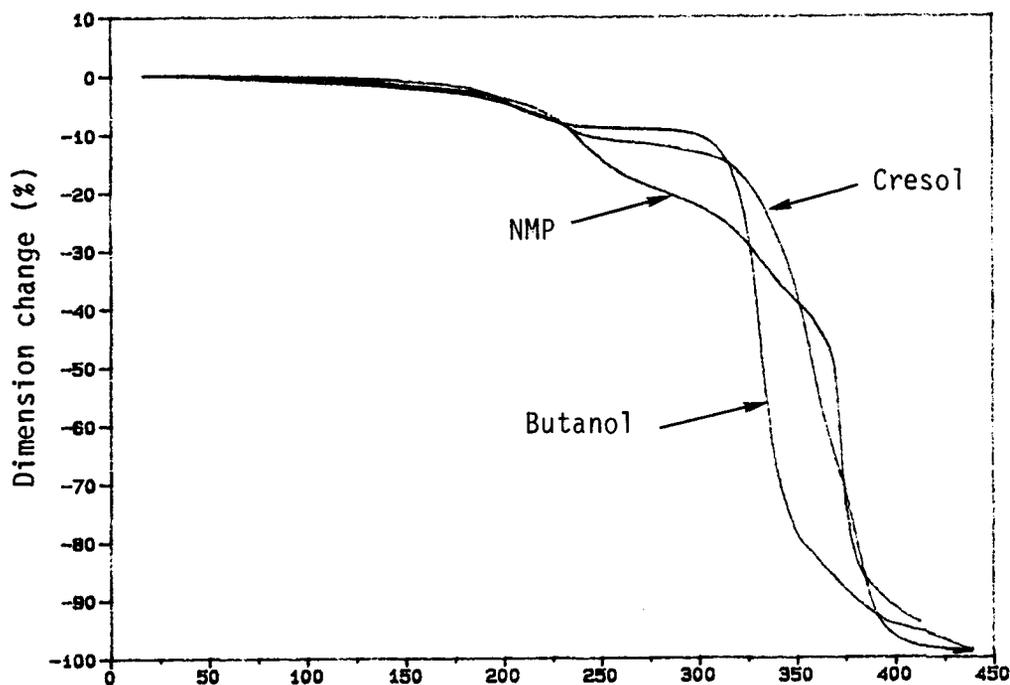


Figure C-3. Flow curves of cresol-evaporated samples of BTDA/BAC/m-PDA/PA polymer

Evaporation of the cresol from samples withdrawn from the near-clear reaction gave some opacity. The majority of the polymer was isolated with methanol treatment, and after drying for 16 hr at 200°C under high vacuum, a molding was prepared which was visually clear. Small portions of the powder and the molding were redissolved in cresol at 180°C, the latter with some difficulty.

The DSC curves for the samples indicated below are given in Figure C-4 (in the order shown below):

- (1) Fibrous polymer
- (2) Fibrous polymer molded 30 min at 303°C, 6.9 MPa
- (3) Reaction evaporated to dryness and treated for 1 hr at 329°C
- (4) Fibrous polymer dissolved in cresol, treated the same as No. 3
- (5) Molded polymer dissolved in cresol, treated the same as No. 3

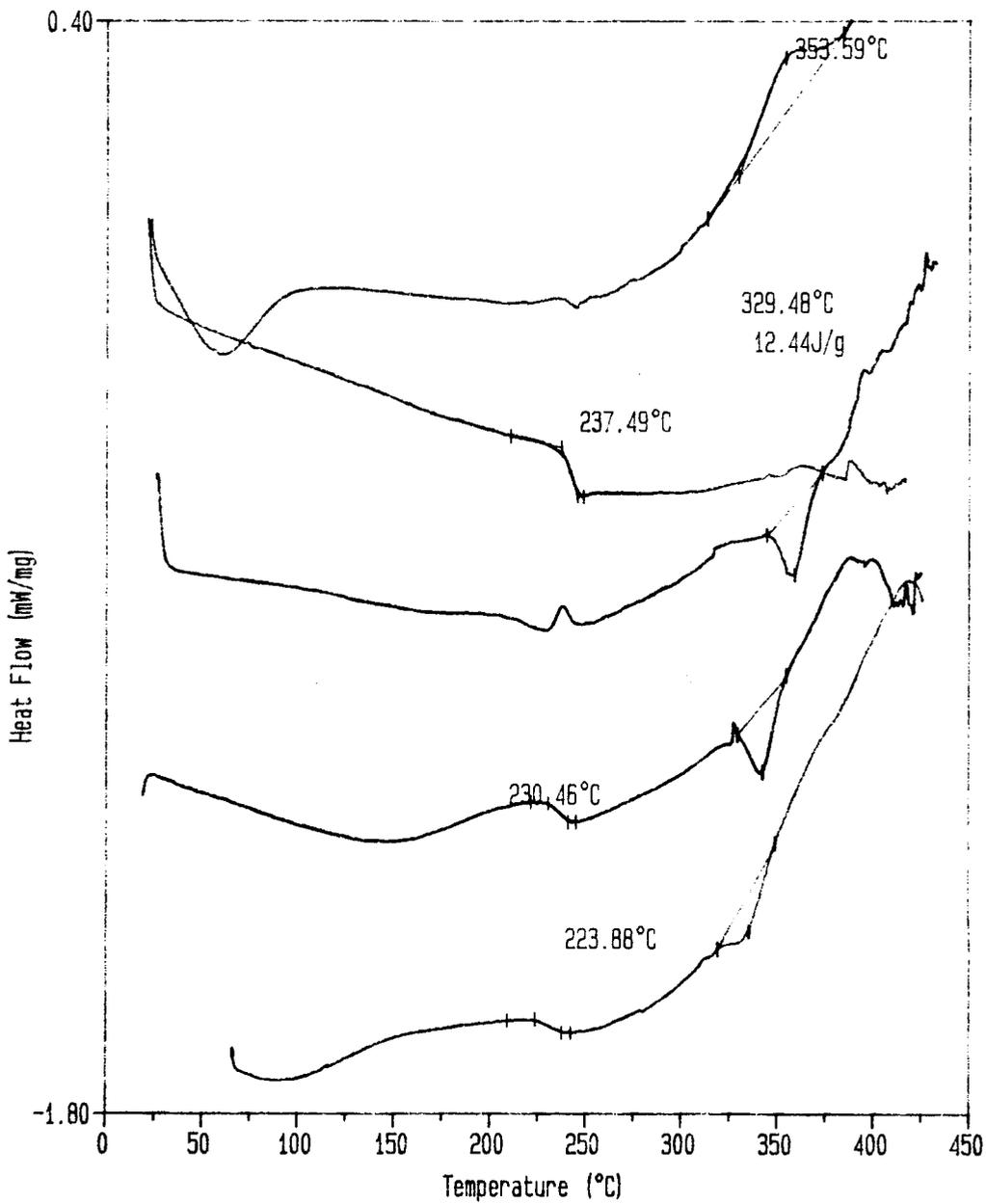


Figure C-4. DSC curves of BTDA/BAC/m-PDA/PA polymers from the same final reaction mixture

Clearly evident in the polymers from cresol evaporation is an endotherm just below to 350°C which was not present in either the neat fibrous polymer or the molding.

Flow curves for Samples 2, 3, 4, and 5 are provided in Figure C-5. Curves were obtained at 0.2 MPa (28 psi) pressure. It is clear that the excellent flow properties of the molded polymer (Sample 2) were compromised by the cresol treatment. This is probably due to crystallinity or other phenomena which gave rise to the endotherms seen in the DSC curves of these polymers in Figure C-4. Flow onset in the cresol-treated polymers is about 50°C higher for all of the cresol-treated polymers than the molded polymer.

Samples of the 329°C treated molded polymer, the reaction mixture, and the fibrous polymer redissolved in cresol were treated for 30 min at 350°C and subsequently for 10 min at 400°C in an air circulating oven. Weight losses

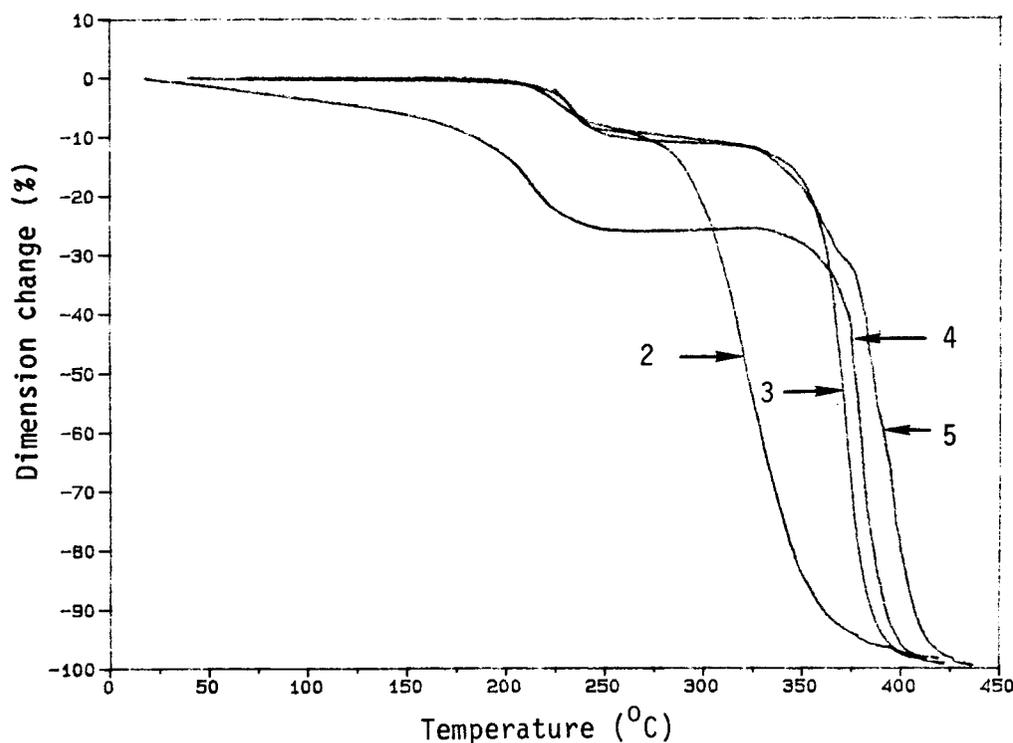


Figure C-5. Flow curves of BTDA/BAC/m-PDA/PA polymers from the same final reaction mixture

for the 1 hr at 329°C treated samples through the 10 min at 400°C treatment for the polymers were 3.1, 16.5, and 3.5 percent, respectively. The origin of the volatile species is not clear, but may include absorbed atmospheric moisture, residual unreacted monomers, cresol, and methanol. The onset Tgs by DSC after the 350°C treatment were 235°C, 229°C, and 225°C, respectively. After 400°C treatment, the values were 235°C, 239°C, and 225°C, respectively. The variation in final Tgs is not understood, particularly between the molded polymer and the fibrous polymer.

Flow curves for the three polymers heated at 350° and 400°C are provided in Figures C-6 and C-7. Both of the polymers isolated by cresol evaporation show that the 350°C treatment temperature is inadequate to improve the flow properties over the beginning 329°C treated samples. The DSC's of these two materials show an increase in the endotherms with treatment at this temperature. Treatment of these two polymers at 400°C shows improved flow properties and loss of the endotherm by DSC analysis. Some amount of polymer decomposition may have occurred with the 400°C treatment. The flow properties of the molded specimen were modified slightly with the thermal treatments as noted in the top diagram of Figure C-6. Included in this diagram is the flow curve of the molded polymer.

C.3 SUMMARY OF FINDINGS

Relevant to program goals, the flow curves of BTDA/m-PDA/BAC polyimides obtained by cresol evaporation are probably unacceptable. The flow curves suggest that a high-temperature treatment schedule might be devised to eliminate the endotherm, however, the program approach required that this can be accomplished on the prepreg and not the neat resin.

It is clear that the opacity developed in the early stages of the reaction is related to the increasing concentration of an intermediate or

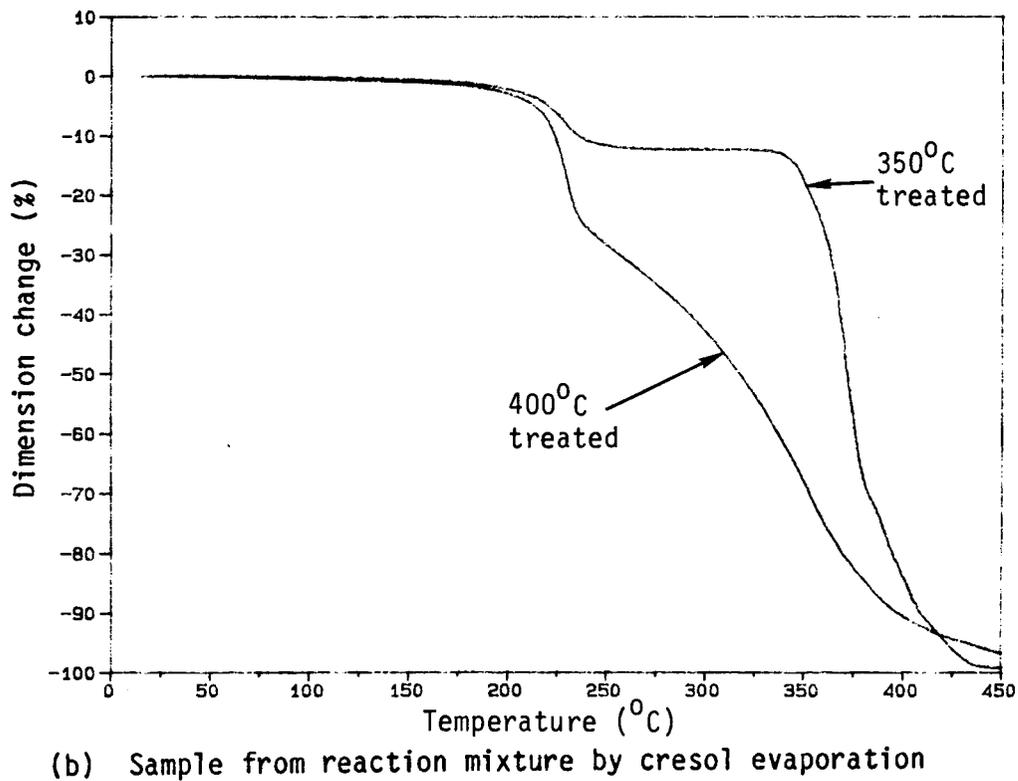
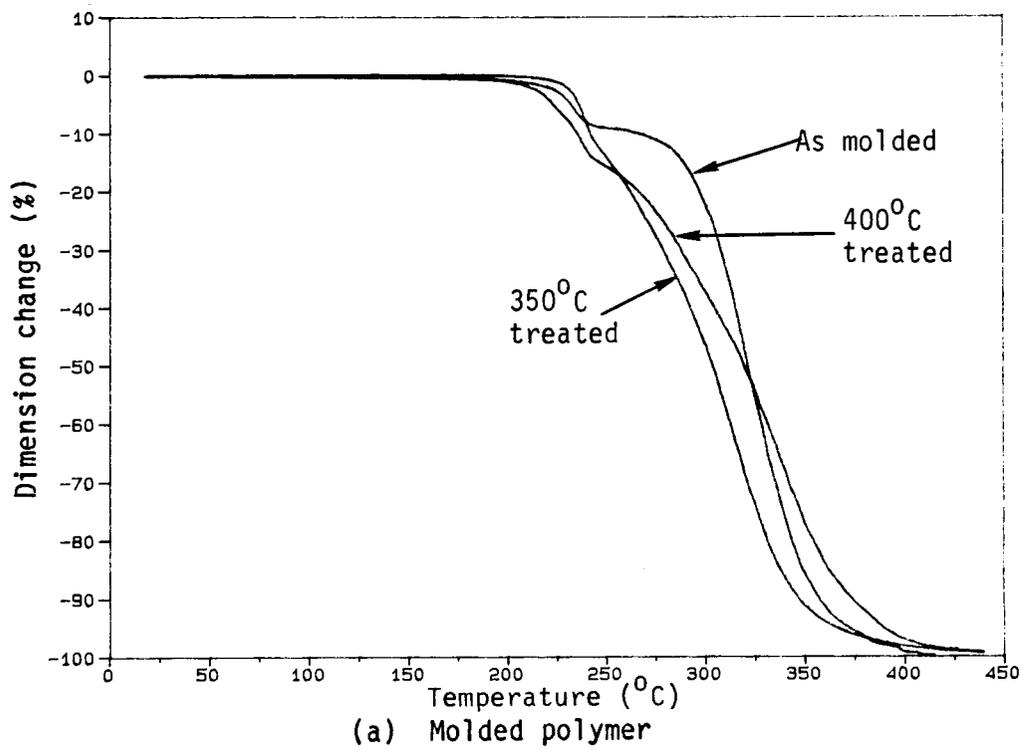
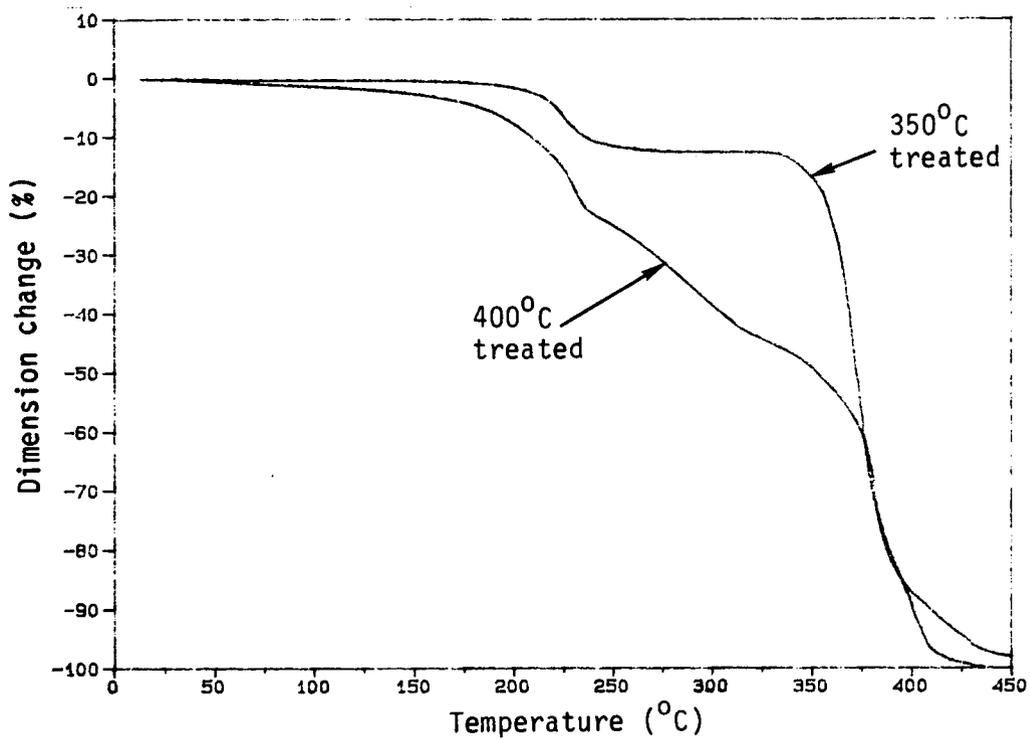


Figure C-6. Flow curve variation of BTDA/BAC/m-PDA/PA polymers with heat treatment



Sample from redissolved fibrous polymer by cresol evaporation

Figure C-7. Flow curve variation of BTDA/BAC/m-PDA/PA polymers with heat treatment

precursor polymer which is insoluble in the cresol. Both the inability to conduct polymerization at 20 percent solids and evaporation of clear cresol solutions to produce opaque samples suggest this. Reactions at 100 percent stoichiometry have a far less tendency to produce opaque samples upon cresol loss than do reactions at lower BTDA or amine stoichiometries. Reactions at 97.5 percent BTDA stoichiometry appear to require longer reaction times than 100 percent stoichiometric reactions to produce samples which upon cresol evaporation do not produce opacity at the same concentration of reactants. Since the reaction rate is monomer-concentration dependent, the reason extended reaction times are required for the phthalic anhydride end-capped polymers is not clear.

Isolations of a few milligrams of cresol insoluble (opacity) material from the NMP-modified cresol reaction occurred by repeated overnight settling of the particles, decanting, and addition of fresh cresol. The powder had a very complex infrared spectrum (carbonyl region) and no visible melting point to 450°C. DSC analysis showed an exotherm with a peak temperature of 398°C and a ΔH of 69 joules/gram. Reheat of the sample, which showed about a 10 percent weight loss through the first heating, gave a curve which had an onset Tg of 240°C and no high-temperature exotherm. This experiment suggests that opacity is a precursor to the final BTDA/BAC/m-PDA composition. The lack of an endotherm in the DSC curve suggested that cresol insolubility may not be due to crystallinity. The endotherm, which influences the flow properties of the polymer, is a direct result of heating cresol solutions of the polymer for 1 hr at 329°C or higher.

Cresol appears to be a suitable reaction medium; however, cresol alone appears to be an unsuitable prepregging solvent. Further, no cosolvents, such as butanol, were found to be useful in eliminating the high-temperature

endotherm which alters the flow properties. Methanol treatment appears to be very effective in removing something from the cresol reaction mixture which causes high weight losses upon heating from 325°C to 400°C. This high weight loss may be cresol, however, after resolution of the methanol-treated polymer with cresol, its weight loss is consistent with expectation -- specifically, the same as the starting polymer.



Report Documentation Page

1. Report No. NASA CR 178413		2. Government Accession No.		3. Recipient's Catalog No.	
4. Title and Subtitle Development of an Impact- and Solvent-Resistant Thermoplastic Composite Matrix -- Phase IV				5. Report Date September 1987	
				6. Performing Organization Code	
7. Author(s) C. B. Delano				8. Performing Organization Report No.	
				10. Work Unit No. 534-06-23-02	
9. Performing Organization Name and Address Acurex Corporation/Aerotherm Division 555 Clyde Avenue, P.O. Box 7555 Mountain View, California 94039				11. Contract or Grant No. NAS1-16808	
				13. Type of Report and Period Covered Contractor Report	
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Langley Research Center Hampton, Virginia 23665-5225				14. Sponsoring Agency Code	
15. Supplementary Notes Langley Technical Monitor: P. M. Hergenrother, NASA-Langley Research Center, Hampton, Virginia 23665					
16. Abstract Polyimides from BTDA with m-phenylenediamine and three aliphatic diamines were prepared in cresol and characterized. Characterization tests included compression strength and modulus, stressed solvent resistance, and melt-flow tests. Efforts to reduce the molecular weights of these polymers by either stoichiometric imbalance or phthalic anhydride end capping produced opacity in the polymer moldings when the stoichiometry was less than 99 percent. Use of 2,4-diaminotoluene in place of the m-phenylenediamine allowed clear polymer moldings to be obtained at all stoichiometries by end capping or stoichiometric imbalance. After melt-flow/molecular-weight studies, carbon fabric composites were prepared from three polyimide compositions containing BTDA, 2,4-diaminotoluene and two aliphatic diamines. Flexural strengths of two of the resins were in excess of 689 MPa (100 ksi) at both room temperature and 93°C. The polyimide from BTDA, 1,6-hexanediamine, 1,3-bis(aminomethyl)cyclohexane and 2,4-diaminotoluene was selected for scale-up and neat resin characterization tests. The Tg of this polymer was 233°C.					
17. Key Words (Suggested by Author(s)) Aliphatic Polyimides Physical Properties Prepregs Composites Mechanical Properties			18. Distribution Statement Unclassified -- Unlimited Subject Category 27		
19. Security Classif. (of this report) Unclassified		20. Security Classif. (of this page) Unclassified		21. No. of pages 124	22. Price